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OXIDE CERAMIC FIBERS BY THE SOL-GEL METHOD

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Sol-gel processing has many advantages over traditional powder based ceramic processing. These advantages include better homogeniety, higher purity and low temperature synthesis. Additionally, the sol-gel process is the only low temperature process available to make high temperature stable oxide fibers. Most of these fibers cannot be formed by drawing via the traditional melt method. This report includes research conducted on the preparation of lanthanum chromite fibers. Lanthanum chromite's high temperature stability in an oxidizing atmosphere was also investigated. The stability was enhanced by coating with alumina. Additionally, a test rig was developed to measure the mechanical properties of fibers at high temperatures. Several commercial fibers, including alumina fibers were tested with this rig.

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EXECUTIVE SUMMARY

The future development of high temperature composites for structural applications depends on the availability and quality of thermally stable, oxidation resistant fibers. In this project the preparation, thermal stability, and testing of ceramic fibers was investigated. In particular, lanthanum chromite was prepared via the sol-gel route, the thermal stability of commercial lanthanum chromite was studied, and high temperature mechanical testing capabilities for ceramic fibers were established.

The preparation of lanthanum chromite was initially attempted using commercially available chemicals. Although powders and small monoliths were prepared, it appeared that fibers could not be drawn from any of these solutions. At this stage lanthanum hydroxide, lanthanum acetate, and chromium acetate were dissolved in various solvents, including isopropyl alcohol, 1 N HCl, and 1 N HNO_3 to produced small gel samples. The solution consisting of lanthanum hydroxide and chromium acetate in 1 N HNO_3 was modified varying the pH of the solvent. The modification of pH, using NH_4OH, allowed for the control of the polycondensation reaction. This control enabled the preparation of clay-like gel that could be molded into small fibers/rods.

Because the commercially available chemicals could not yield fibers directly from solution, lanthanum isopropoxide was prepared as the basis for several solution systems. The preparation of lanthanum isopropoxide is very tedious as its precursors, $LaCl_3$, La, isopropyl alcohol, and sodium isopropoxide are extremely hygroscopic. Additionally, lathanum isopropoxide is extremely unstable in solution, thus a stock solution could not be prepared. Instead the alkoxide had to be prepared for each experiment individually. The instability of the lanthanum alkoxide in solution is attributed to its hygroscopicity. This hygroscopicity renders all commercially available lathanum isopropoxides insoluble due to a small degree of hydrolysis and polycondensation. Other lanthanum and chromium alkoxides are reportedly insoluble due to their chemical nature.

The prepared lanthanum isopropoxide was teamed with chromium pentanedionate and chromium 2-ethylhexanoate to produce lanthanum chromite precursor gels. By controlling the processing steps in the lanthanum alkoxide and chromium 2-ethylhexanoate system, long continuous fibers could be drawn from the solution. Upon firing, these fibers were fragile due to their porosity. Scanning electron micrographs showed the as drawn surface and the fracture surface. A preliminary Time-Temperature-Transformation curve was drawn using differential scanning calorimetry results.

The thermal stability of lanthanum chromite had been previously studied. However, the development of the KERAMAX lanthanum chromite furnace by FUJI SHO mandated an additional investigation. A lanthanum chromite heating element was purchased and dissected. It became evident that the lanthanum chromite in the heating element was no more stable than any other lanthanum chromite, but that the longevity of the element was increased by an engineering solution. The inside of the heating elements are packed with chromium oxide. As the chromia evaporates from the surface it is replaced by the inner reservoir of chromia.

To increase the lanthanum chromites thermal stability a sol-gel derived coating of alumina was placed on some pieces of the heating element. Aluminum di(sec butoxide) acetoacetic ester chelate in dry isopropyl alcohol was used to dip coat the pieces. This alumina coating significantly reduced the vaporization rate of chromium oxide at 1500°C and 1600°C in air. The reaction between the alumina and lanthanum chromite was investigated using a reaction couple. The chromium and lanthanum diffused into the alumina, however no interdiffusion of the aluminum into the lanthanum chromite occurred.

In addition to the characterization and preparation of lanthanum chromite, the ability to measure a fibers mechanical properties at elevated temperatures was developed. A miniature tensile testing machine housed within a high vacuum system was constructed. Using a specially designed heating element, fiber tensile tests up to 1300°C were performed. The capability of the setup to 2000°C was demonstrated.

As the third facet of the project was to mechanically test the fibers prepared, it became necessary to obtain commercial fibers to test the designed setup. The tensile properties of several types of fibers were measured. The fibers measured included two alumina fibers, one from Mitsui Mining and one from DuPont. Additionally, a carbon fiber and the Tyranno fiber made by Ube were investigated.

Although this project did not yield dense, mechanically strong, stable high temperature lanthanum chromite fibers, significant progress was made in each section of work leading to this final goal. Lanthanum chromite was prepared by several different methods, with one optimized solution resulting in long continuous lanthanum chromite precursor fibers. The thermal stability of lanthanum chromite was reevaluated and enhanced by alumina coating. The ability to mechanically test fibers at elevated temperatures was realized.

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1. OBJECTIVE

The objective of this project was to use the sol-gel method to prepare a ceramic oxide fiber which could be chemically and mechanically stable above 1650°C and preferably up to 2000°C in an oxidizing atmosphere. Equipment and test methods were designed to measure the relevant properties of the fiber at these elevated temperatures. If creep should occur at high temperatures dopant additions were to be made to decrease creep. This report includes research progress made between December 1986 and February 1988.

2. BACKGROUND

The use of ceramic parts in gas turbine engines has many advantages over conventional parts, such as higher operating temperatures, improved fuel efficiency, reduced weight and greater thrust -to -weight ratio. Using ceramic materials also decreases the dependence on strategic materials. Ceramics are inherently less dense than metallic alloys while they retain their strength at higher temperatures. Because of their bonding, most monolithic ceramics are brittle and lack fracture toughness. As demonstrated in ceramic engine parts, these characteristics have led to catastrophic failure due to point contact stresses.

Recently developed fiber-reinforced ceramic matrix composites offer the promise of overcoming these problems. The fracture toughness for these composites is significantly higher than for monolithic materials. Unfortunately, the strength, fracture toughness, and/or oxidation resistance of these current generation composites deteriorate rapidly above about 1000°C. In fact, there is no structural reinforcement material currently available for use above approximately 1200°C.

The sol-gel method of producing ceramics from metallo-organic precursors allows for the precise control of composition, microstructure and product shape. In the design of high temperature oxide fibers the sol-gel method is useful because fibers can be drawn directly from the solution at room temperature. The fiber can then be crystallized at relatively low temperatures. The solution chemistry variables, which must be controlled to arrive at this final crystalline fiber,

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include: precursors, solvent and catalyst type, their concentrations, and solution viscosity. In addition, the processing variables of aging, drying, and firing must be controlled to achieve a final small grained, dense fiber.[1,2]

Many crystalline oxides have been made via the sol-gel method as listed in Table 1. As shown, ZrO_2 and TiO_2 as well as others have been made into fibers and monoliths. Not surprisingly, glassy fibers have been made from gels as shown in Table 1. Preparing any ceramic via the sol-gel method is possible, as long as the precursors are available. Listed in Table 2 are the candidates (dependent on availability of precursors).[18] Aluminum oxide fibers which are commercially available are known to undergo creep at temperatures in excess of 1400°C.[19] Since the melting temperature of Al_2O_3 is 2045°C, as a first approximation, consideration was given only to those oxides with melting points higher than Al_2O_3.

Although the melting temperature of a material is a critical parameter for high temperature applications, other materials characteristics are as important. One of these characteristics is the lack of phase transformations. Two oxides with detrimental phase transformations are zirconia and hafnia. Even though their melting points are ~2715°C and ~2812°C, respectively, the phase transformation from tetragonal to cubic causes mechanical degradation rendering them useless in high temperature applications. These phase transformations can be suppressed in binary syste ns such as CaO-stabilized zirconia. In fact, a number of stabilized zirconates and hafnates exist which have liquidus temperat ires well in excess of 2000°C. Because the resultant crystal structures are known to have significant concentrations of oxygen vacancies, it is likely that creep will occur at temperatures in excess of 1650°C. Thus such binary solid solutions were eliminated from consideration .

If creep should occur in any system at elevated temperatures, it is possible that it can be minimized via the dispersion of particulates in the fiber. Oxide fibers for use in composite systems will typically have a diameter of less than 15 microns. This fiber size limits the particle diameters to less than 1 micron. Secondly, the dispersed phase should not react chemically with

Table 1 Examples of oxides prepared by the sol-gel method.

	Monoliths	Film	Fiber	Reference
Polycrystalline				
Al_2O_3	X	X	X	3
$Al_2O_3 \cdot SiO_2$	X	X		3
$Al_2O_3 \cdot GeO_2$	X			4
$Al_2O_3 \cdot Y_2O_3$	X			5
$Li_2O \cdot Fe_2O_3$	X			6
MgO	X			7
Ta_2O_5	X			8
ThO_2	X			9
TiO_2	X		X	10
$2TiO_2 \cdot 5Nb_2O_5$	X			11
Y_2O_3	X			12
ZrO_2	X		X	13
Glassy				
$ZrO_2\text{-}SiO_2$	X	X	X	3
$TiO_2\text{-}SiO_2$	X	X	X	3
SiO_2	X	X	X	3
$CaO\text{-}Al_2O_3\text{-}SiO_2$	X			14
$GeO_2\text{-}PbO$	X			15
$K_2O\text{-}SiO_2$	X			16
$Na_2O\text{-}SiO_2$	X			17

Table 2 List of candidates for fibers via the sol-gel method.[18]

Oxide Temp. System	Density (g/cc)	Melting Temp. (°C)	Dispersed Phase	Melting Temp. (°C)
$LaCrO_3$	6.69	2500		
$LaAlO_3$		2100		
Sr_2ZrO_4		2200	SrO	2420
Al_2O_3	3.97	2045	$SrO \cdot Al_2O_3$	1900
Cr_2O_3	5.21	2275	$LaCrO_3$	2500
MgO	3.58	2800	$3MgO \cdot Y_2O_3$	2150
SrO	4.70	2415	Sr_2ZrO_4	2200
Y_2O_3	5.01	2410	Y_4GeO_8	2000
CeO_2	7.13	2600		

the matrix, nor should there be mutual solubility. Solid solutions of different chemical compositions are not acceptable. A compound in contact with a solid solution in which it is one of the constituents is also unacceptable. However, two compounds which do not form solid solutions can be considered.

Table 2 shows a list of possible oxide systems with melting points greater than that of alumina. Magnesium oxide with a melting point of 2800°C was eliminated because it has been shown to creep above 1600°C.[20] The next two oxides with the highest melting points are ceria and lanthanum chromite. Thus, lanthanum chromite was chosen over ceria because it is available commercially in polycrystalline rod-form and is used at temperatures in excess of 1800°C for very long periods of time.

3. RESEARCH PERFORMED

The research performed was directed in three parts. The first part was the preparation of high temperature, stable ceramic fibers, namely lanthanum chromite fibers, by the sol-gel method. The second part was the investigation of lanthanum chromite's thermal stability, including ways to enhance its thermal stability in an oxidizing atmosphere. The investigation of lanthanum chromite's thermal stability is essential for the development of composites utilizing lanthanum chromite fibers. The third part was the testing of the high temperature mechanical properties of fibers. This focused on the design of a test rig.

3.1   Lanthanum Chromite Preparation

Previously, lanthanum chromite was prepared by traditional powder processing[20] or by the amorphous citrate method.[21] Neither technique allows for the preparation of fibers or bulk pieces. By manipulation of the solution chemistry the sol-gel method can produce powders, monoliths, fibers and films. Preparing lanthanum chromite via the sol-gel method would establish a new process for making lanthanum chromite and demonstrate the potential for

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formation of lanthanum chromite fibers. When making a product via the sol-gel method, each step must be controlled and its effect on the final product evaluated. The first step is to produce a homogeneous solution containing, in our case, lanthanum oxide precursors and chromium oxide precursors. These precursors are then hydrolyzed and polymerized to form a viscous solution. By controlling the viscosity-time relationship either monolithic pieces can be formed or a fiber can be drawn or spun from solution. This investigation was to establish feasibility of fiber formation, thus fibers were drawn from the solution instead of spun. After formation into fibers or monoliths the sample is subsequently dried and fired. The procedure is outlined in the flowchart in Figure 1.

Figure 2 shows the proposed technical approach. As seen in this figure there are four phases of the program. Phase 1 goes from a homogeneous solution to small gel pieces and requires only gel formation before firing and $LaCrO_3$ formation after firing. Phase 2 also begins with a homogeneous solution but the solution viscosity must be controlled to enable the formation of short gel fibers. These fibers in turn are fired to form crystalline $LaCrO_3$. Both Phase 1 and Phase 2 were followed through the characterization step. During this stage the gel or fiber was analyzed by X-ray diffraction and scanning electron microscopy. The lack of mechanical strength of the sample did not allow for testing. The work done via Phase one and two are discussed in Sections 3.1.1 and 3.1.2, respectively. Phase 3 is then the optimization of the solution to yield continuous or long discontinuous fibers. After Phase 1 and 2 were conducted with commercially available chemicals, they were redone with lanthanum alkoxide solutions prepared at UCLA. These lanthanum alkoxide based solutions were then optimized leading to Phase 3. Continuous fibers upto 20 inches long were hand drawn and characterized. Phase 4 was to be considered if the fiber's final mechanical properties were unsatisfactory. As the mechanical properties were not tested, the addition of dopants was not attempted. However
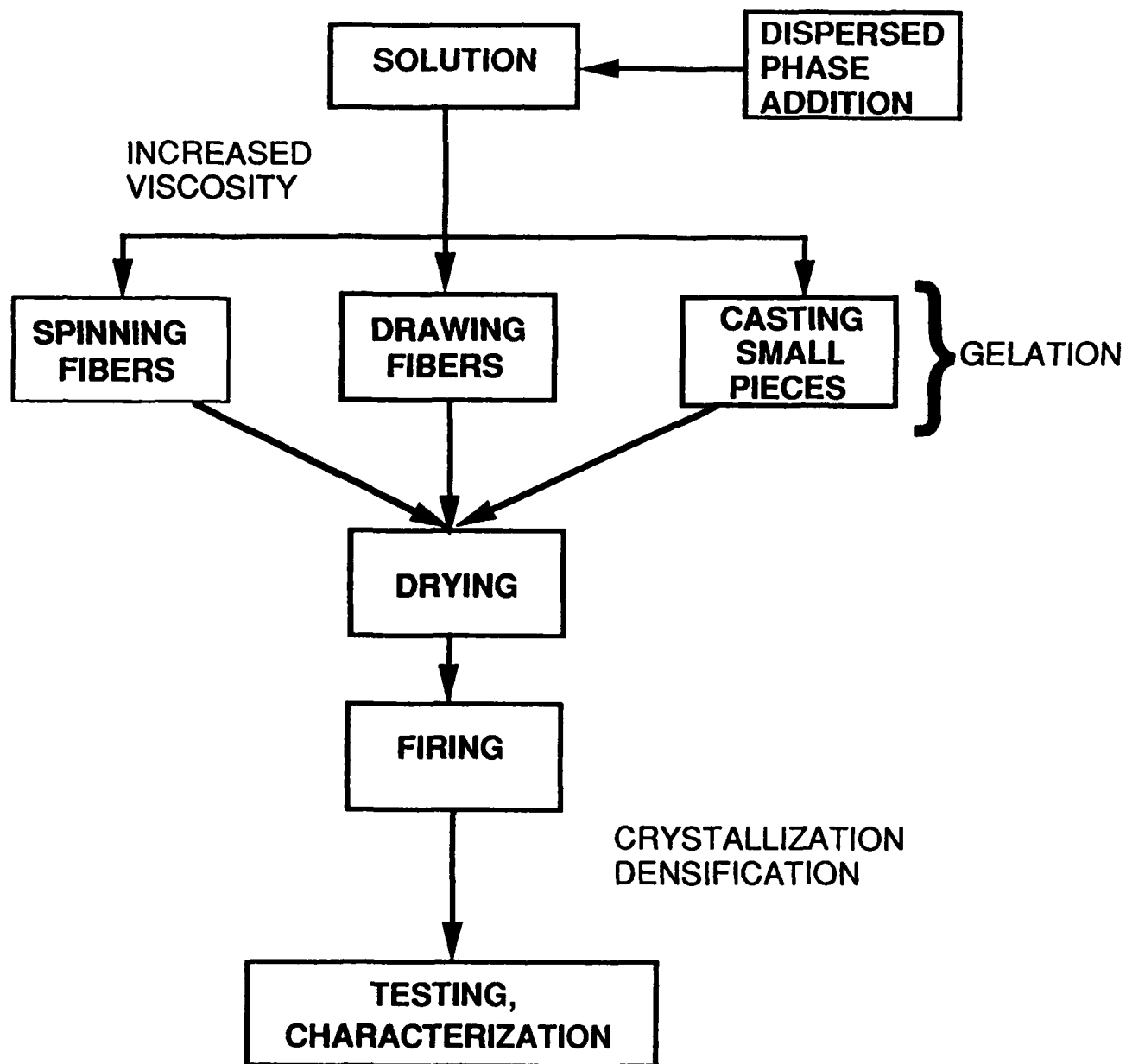
Figure 1. General flowchart of preparation procedure for sol-gel processing

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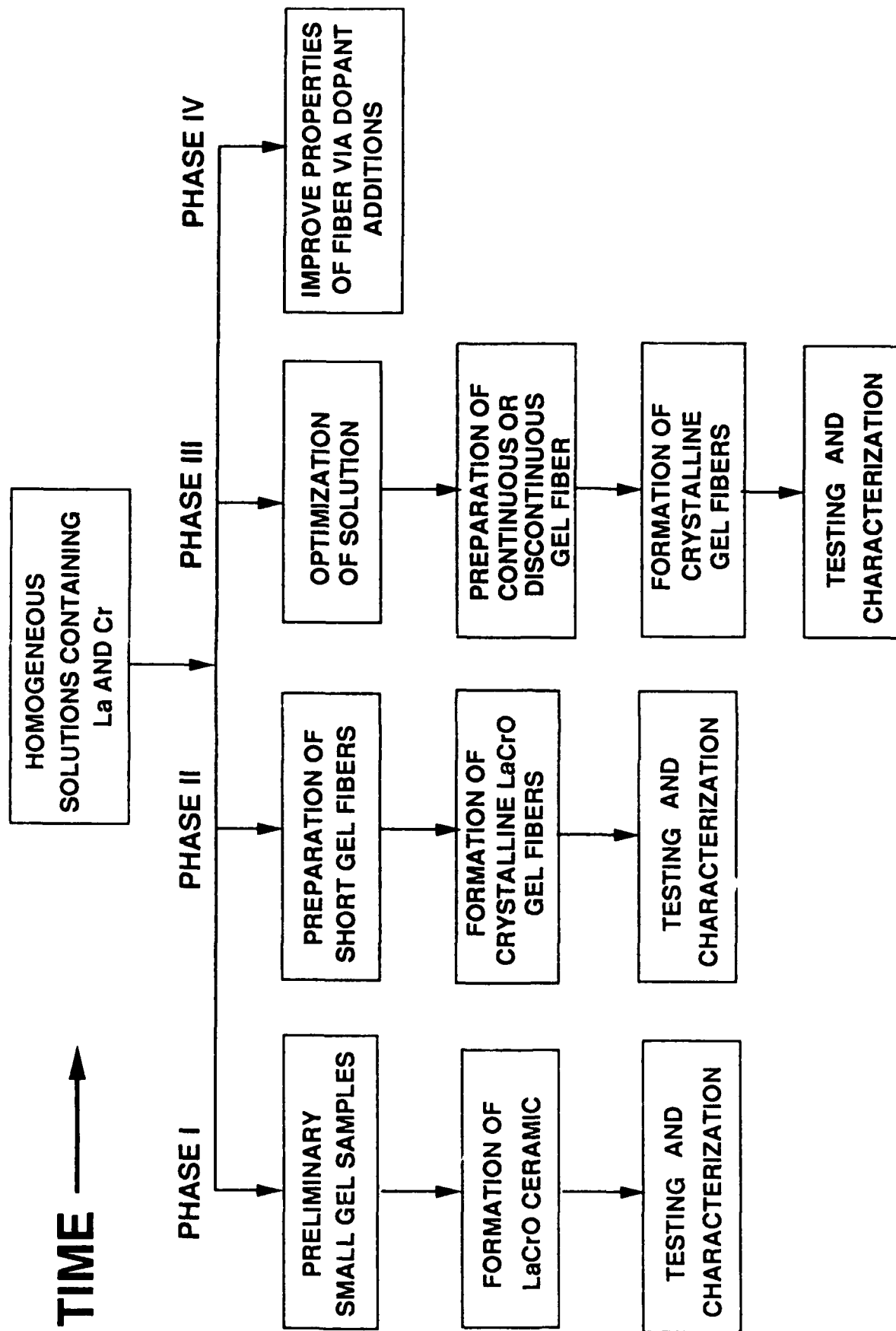
Figure 2.   Proposed technical approach for the preparation, characterization and testing of lanthanum chromite fibers.

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in this theoretical case, dopants produced via the sol-gel route could have been added to the homogeneous solution. The results obtained from each phase are described in the following sections.

3.1.1 Synthesis of Lanthanum Chromite Using Commercially Available Precursors

The proper selection of precursors, solvents and catalysts is critical in gel preparation.[23,24,25] First, creating a homogeneous solution containing lanthanum and chromium metallo-organics is not a trivial task. It is at this point that the gel characteristics are established, which ultimately control the ceramic materials properties. In doing work on an unknown system, such as lanthanum chromite, many solutions should be investigated. By identifying the available organo-metallic precursors for lanthanum oxide and chromium oxide and coupling them with common solvents and catalysts an experimental test matrix was generated. The raw materials, catalysts, and solvents investigated in this program are listed in Table 3. By varying the different raw materials, solvent, and catalyst combinations, the two solubility tables shown in Table 4 and Table 5 were constructed.

The compatible lanthanum precursor solutions and chromium precursor solutions combinations were then mixed. These were allowed to hydrolyze and polycondense to form gels. Only three systems were found to produce homogeneous solutions whose viscosity increased leading to gelation. Figure 3 shows an outline of the selection criteria at each step. If at any point precipitation or immiscibility occurs the solution system was rejected. An additional reason for rejection was the lack of increase in viscosity. This occurred in four systems. In these cases the solution viscosity did not appear to change over time. The three successful systems are outlined in Figure 4 , Figure 5, and Figure 6 . Figure 4 shows the procedure for making a gel from lanthanum hydroxide dissolved in 1N hydrochloric acid and chromium acetate dissolved in isopropyl alcohol. This procedure yielded mixed phases at 1000°C. Figure 5 shows

Table 5   Solvents, raw materials and catalysts considered in making lanthanum chromite.

RAW MATERIALS

Lanthanum Acetate	$La(OOCCH_3) \cdot 1.5H_2O$
Lanthanum Isopropoxide	$La(OC_3H_7)_3$
Lanthanum Hydroxide	$La(OH)_3$
Lanthanum 2,4-Pentanedionate	$La(CH_3COCHCOCH_3)_3$
Chromium(III) Acetate	$Cr_2(OCOCH_3)_4 \cdot 2H_2O$
Chromium(II) 2-Ethyl Hexanoate	$Cr(C_8H_{15}O_2)_3$
Chromium(II) Hydroxide	$Cr(OH)_3$
Chromium(III) 2,4-Pentanedionate	$Cr(CH_3COCHCOCH_3)_3$

SOLVENTS

Acetonitrile	CH_3CN
Acetone	C_3OH_6
Benzene	C_6H_6
2-Ethyl Hexanoic Acid	$CH_3(CH_2)_3CH(C_2H_5)CO_2H$
Ethylene Glycol	$HOCH_2CH_2OH$
Isobutanol	C_4H_8OH
Isopropanol	C_3H_7OH
2,4-Pentanedione	$CH_3COCH_2COCH_3$
Water	H_2O

CATALYSTS
Citric Acid, HCl, HNO_3, NaOH, NH_4OH

Table 4: Solubility of lanthanum metallo-organic precursors. S defined as 0.2 grams in solution of 10 ml at room temperature.

Solvents	La Hydroxide	La Acetate	La 2,4-pentanedionate	La Isopropoxide Acetonitrile
Acetone				
Acids				
Citric	S	S	S	
HCl	S	S		
HNO$_3$	S	S		
Water		S		
Bases				
NaOH				
NH$_4$OH				
Benzene				
Butanol				
2-Ethyl Hexanoic		S	S	
Ethylene Glycol				
Isopropanol				
2,4-Pentanedione				

Table 5: Solubility of chromium metallo-organic precursors. S defined as 0.2 grams in solution of 10 ml at room temperature.

Solvents	Cr Hydroxide	Cr Acetate	Cr 2,4-pentanedionate	Cr 2-Ethylhexanoic Acid
Acetonitrile				
Acetone				.
Acids				
Citric		S		
HCl				
HNO3		S		
Water		S		
Bases				
NaOH		S		
NH4OH				
Benzene			S	
Butanol				
2-Ethyl Hexanoic				S
Ethylene Glycol				
Isopropanol		S		
2,4-Pentanedione			S	

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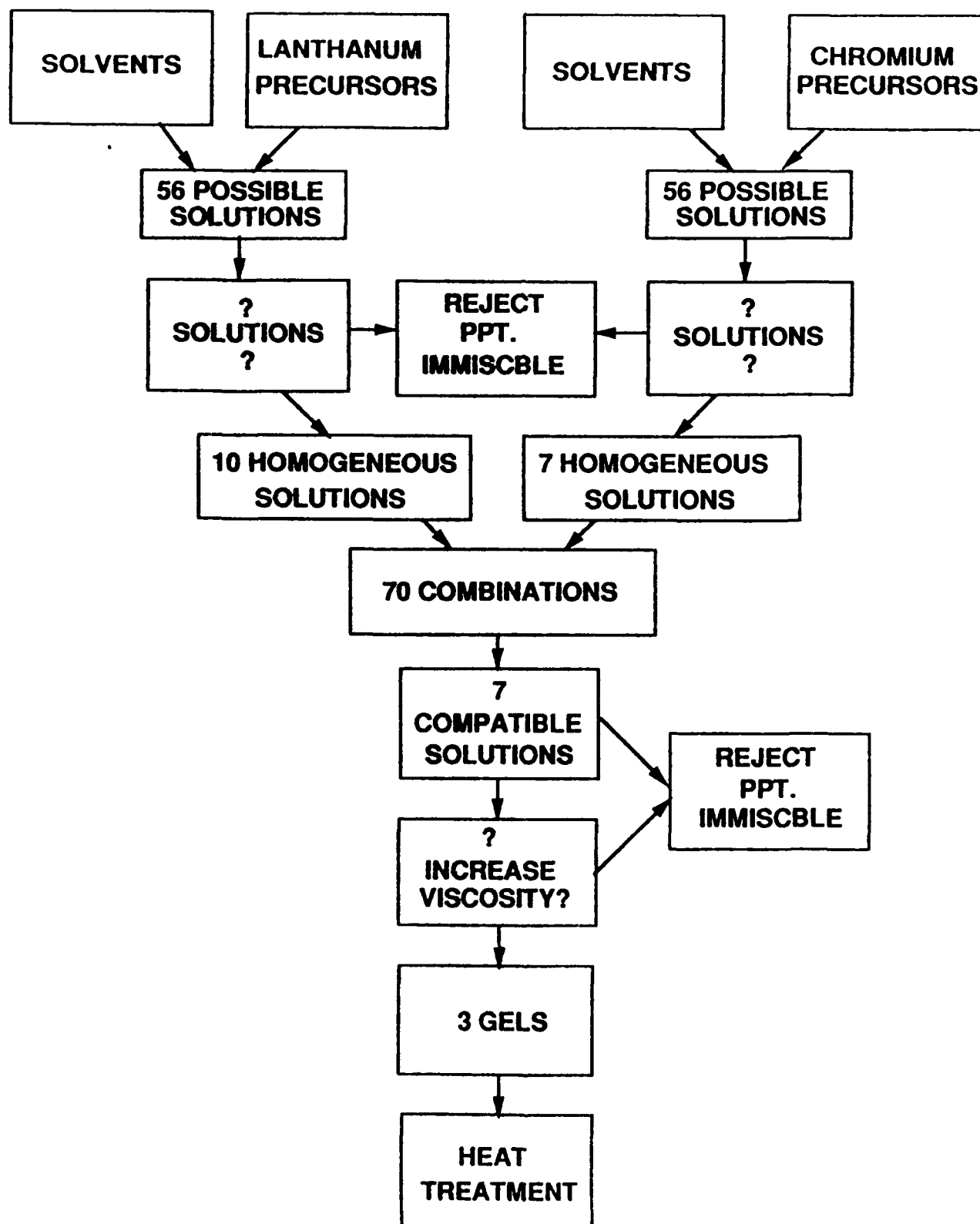
Figure 3. Selection criteria for precursors to prepare lanthanum chromite using commercially available precursors, numbers signify the quantities satisfying the preceding description.
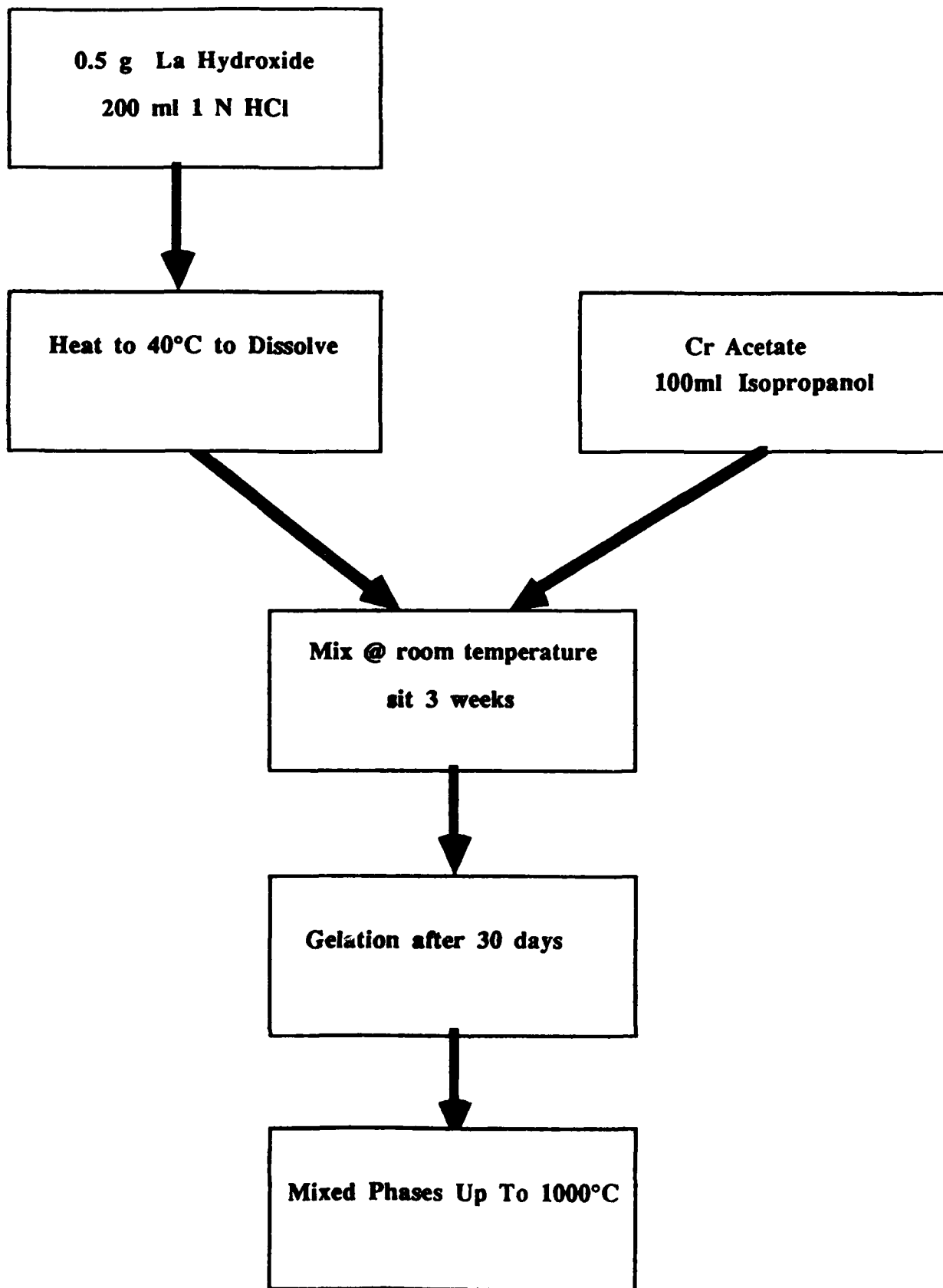
Figure 4. Preparation procedure for lanthanum chromite gel (Gel #1A) from lanthanum hydroxide in 1 N HCl and chromium acetate in isopropyl alcohol.
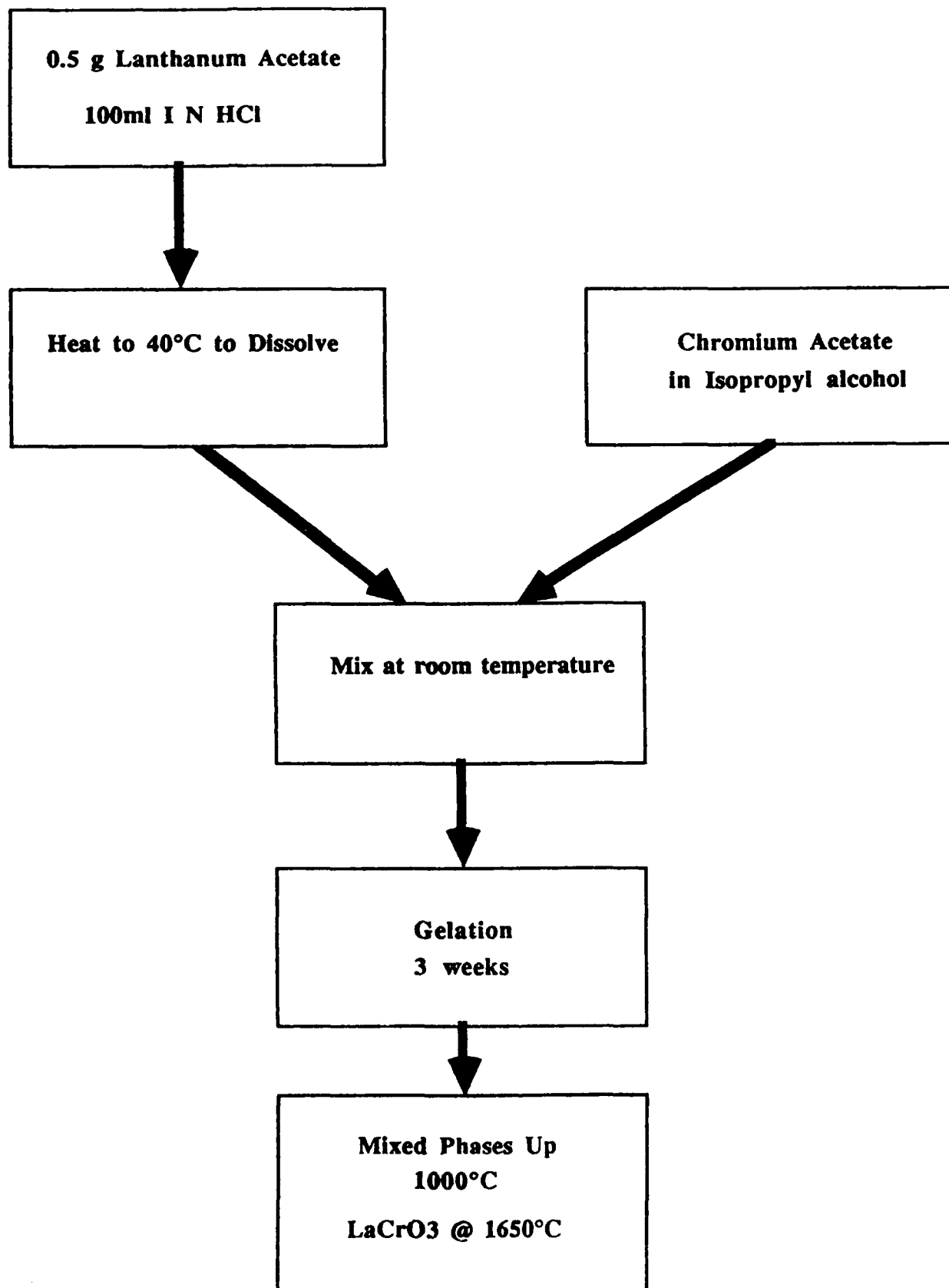
Figure 5.   Preparation procedure for lanthanum chromite gel (Gel #1B)
from lanthanum acetate in 1 N HCl and chromium acetate in
isopropyl alcohol.

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Figure 6.   Preparation procedure for lanthanum chromite gel (Gel #2) from
             lanthanum hydroxide in 1 N nitric acid and chromium acetate in
             1 N nitric acid.The stirring time before mixing was 15 minutes.

the procedure to prepare lanthanum chromite using a similar procedure as in Figure 4, with lanthanum acetate substituted for the lanthanum hydroxide. Again at 1000°C it did not form pure lanthanum chromite. Figure 6 shows the third procedure which passed the selection criteria. In this case nitric acid was used to dissolve both the lanthanum hydroxide and the chromium acetate. Since all the systems included chromium acetate it appears that chromium acetate is the most flexible chromia precursor. The gel formed by the last route was heat treated and characterized by X-ray diffraction at 200°C, 750°C and 1650°C. The X-ray patterns and identification are shown in Figure 7. $Cu_{k\alpha}$ radiation was used with a graphite monochromator. At 1650°C $LaCrO_3$ is the major phase present, along with a small amount of La_2O_3. The lanthanum oxide could be present due to an incomplete reaction of the chromia precursor with the lanthanum oxide precursor at the solution level. The subsequent evaporation of the chromium oxide precursor would result in excess lanthanum oxide in the sample. The lack of solubility of the lanthanum alkoxide resulted in a need to produce precursors which were unhydrolyzed and thus more reactive. These "fresh" precursors would thus be free of hydroxides and polymerization would be minimized.[25] One precursor whose polymerization reaction can be controlled is lanthanum isopropoxide.[26] Because of the lack of availability of soluble commercial lanthanum isopropoxide, it was determined that lanthanum isopropoxide would be prepared to gain greater control over the reaction chemistry. The synthesis method will be discussed in Section 3.1.3

Using commercially available precursors the production of lanthanum chromite via the sol-gel route was demonstrated. Controlling the viscosity of these systems was difficult thus limiting the feasibility of these solutions to yield fibers. The work in this section demonstrates that numerous solution routes exist to produce lanthanum chromite. Powders and small pieces of lanthanum chromite can be formed by these routes. The solutions which passed the selection criteria outlined in Figure 3 the were not fiberizable because the polycondensation reaction could not be controlled.
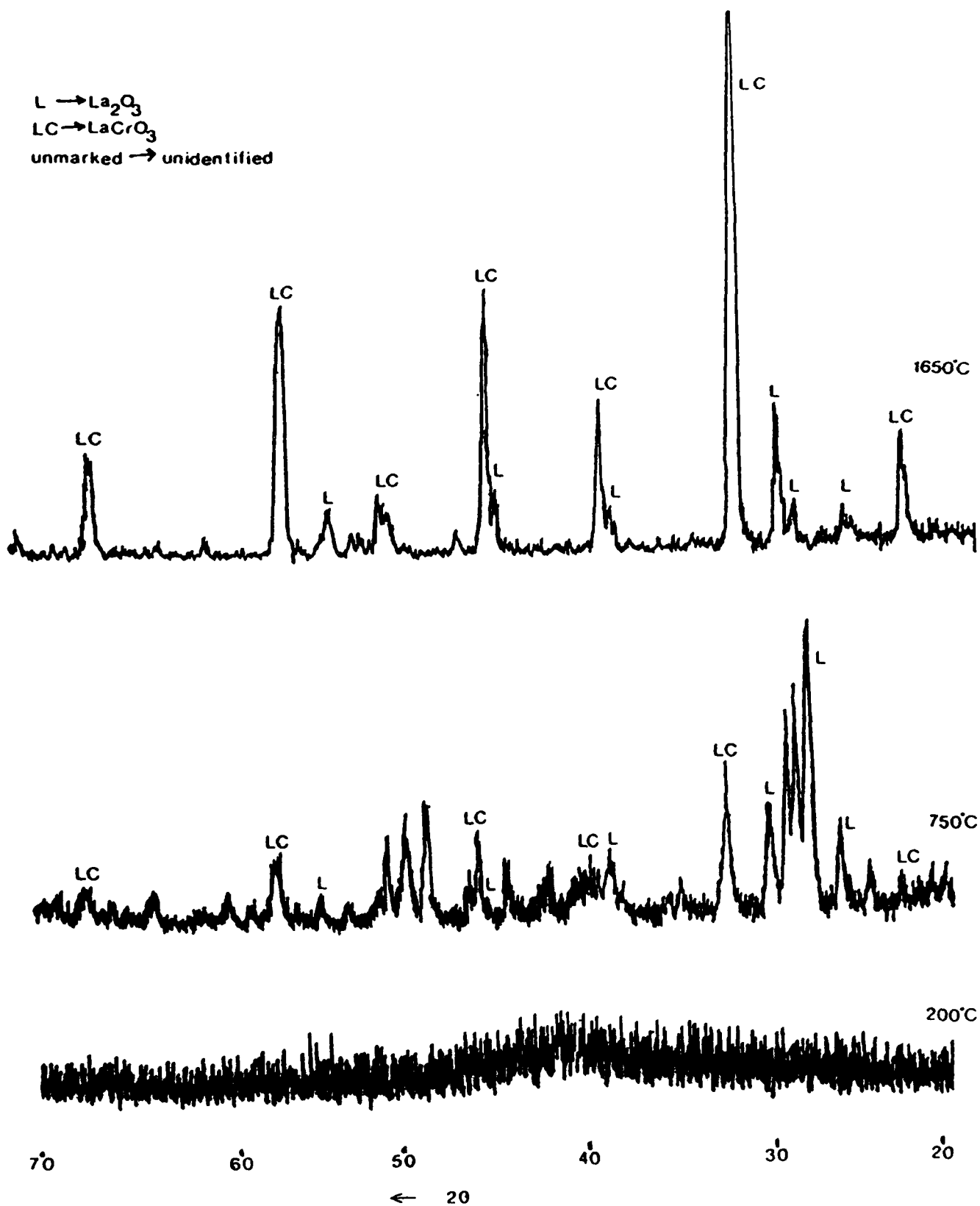
Figure 7. X-Ray diffraction patterns using Cu Kα radiation of the sample (Gel #2) prepared using lanthanum hydroxide and chromium acetate both dissolved in nitric acid and stirred 15 minutes, fired at 200°C, 750°C and 1650°C.

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3.1.2 Modification of Solutions to Obtain Fibers

The next step was to modify the solutions which resulted in lanthanum chromite to control the solution structure and thus viscosity. By controlling the solution chemistry, fibers should be producible.[28,29] From the previous work, gel system number two (Gel #2), in which lanthanum hydroxide and chromium acetate were dissolved in nitric acid, was chosen for further investigation. Previously, the X-ray diffraction pattern of this sample showed La_2O_3 and an unidentified metastable phase. It was found that by dissolving the lanthanum hydroxide more completely, i.e., stirring 30 minutes, instead of 15 minutes the lanthanum oxide and metastable phase would not form upon heating. The flowchart of this procedure is shown in Figure 8. As in the unmodified procedure sample the structure was amorphous at 200°C; however, the modification allowed for the crystallization of single phase lanthanum chromite after heat treatment at 300°C, for 10 hours. The X-ray analysis at 200°C and 300°C is shown in Figure 9.

The X-ray patterns of sample #2 and the $LaCrO_3$ heating element are shown in Figure 10. Although the heating element is doped with 0.0853 weight percent calcium the peak locations are identical. The difference in peak width does illustrate that the sol-gel prepared lanthanum chromite has finer particle size. Further evidence to show that the sol-gel sample has a fine grain size is seen in the SEM micrograph in Figure 11. Thus, the fine grain size of sample #2 resulted from the sol-gel technique and shows promise that the sol-gel produced lanthanum chromite may yield strong, creep resistant fibers. The present problem with the lanthanum chromite, as shown in the SEM, is porosity. Although the porosity was not measured because of the sample's fragility, the porosity appears to be approximately 30 percent and the pore size ranges from 100Å to several microns.

Although sample #2 formed pure lanthanum chromite after firing to just 300°C, the solution viscosity was not high enough to permit fiber drawing. To obtain fibers, the solution chemistry was modified. The modifications which were used on the solution containing lanthanum hydroxide, chromium acetate, and nitric acid were solvent and pH. In all cases the overall
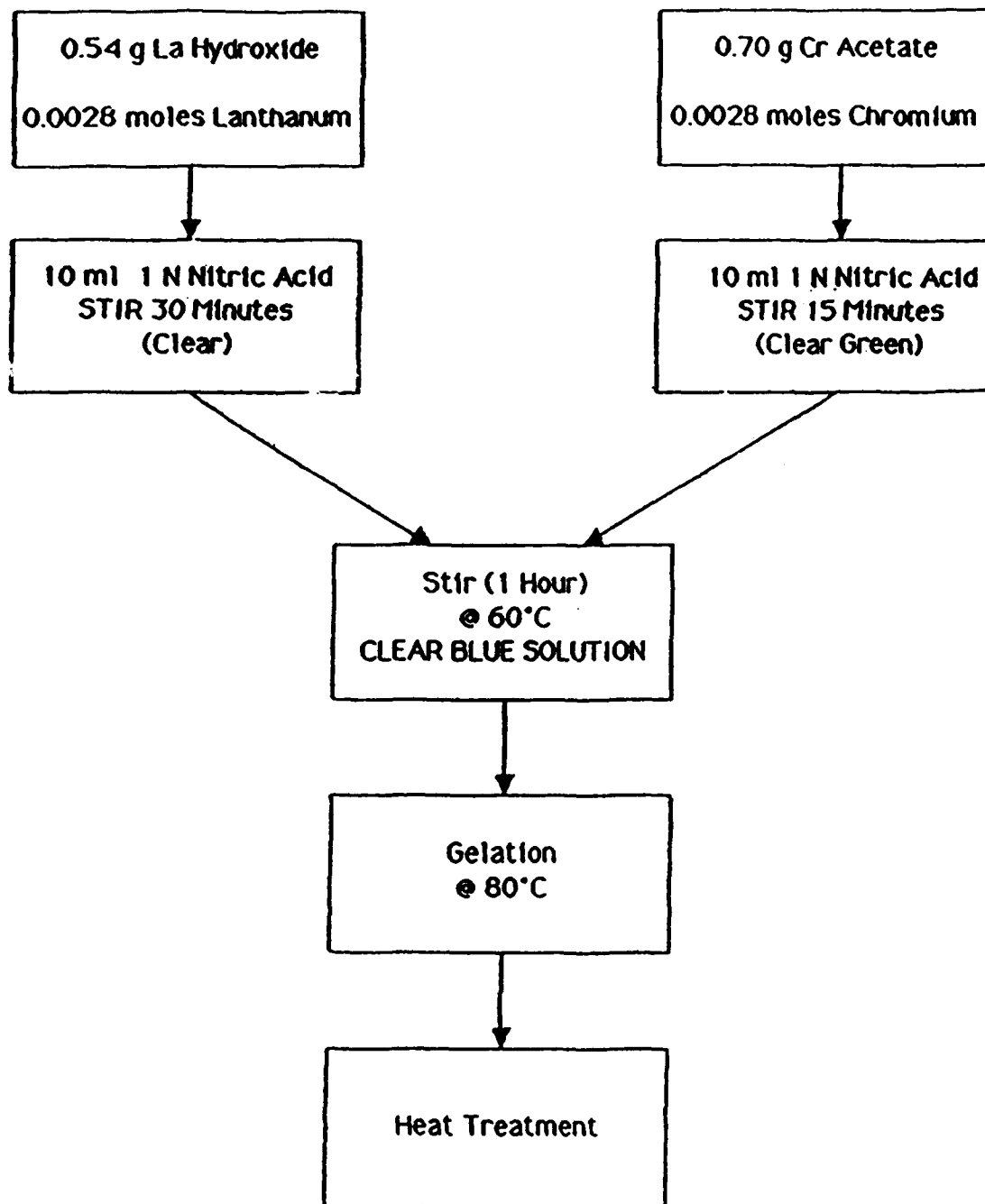
Figure 8.   Preparation procedure for lanthanum chromite gel (modified Gel #2)
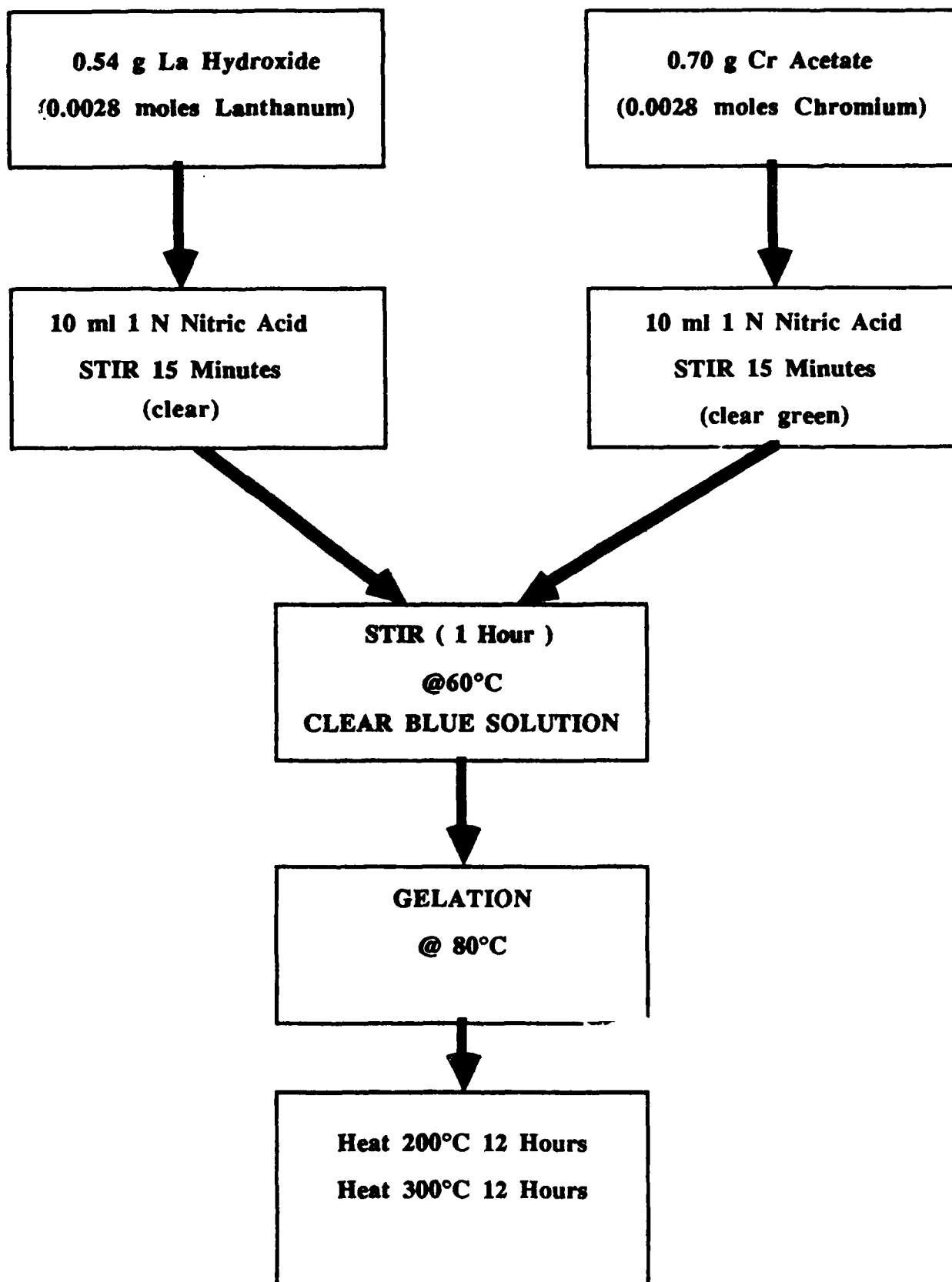from lanthanum hydroxide in 1 N nitric acid and chromium acetate in
1 N nitric acid. The stirring time before mixing was 30 minutes
and 15 minutes, respectively.

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Figure 9.   X-Ray diffraction patterns using Cu Kα radiation of the sample
(modified Gel #2) prepared using lanthanum hydroxide and chromium
acetate both dissolved in nitric acid, stirred 30 and 15 minutes, respectively.
Fired at 200°C and 300°C.

Figure 10. X-Ray diffraction patterns using Cu Kα radiation of the sample
(modified Gel #2) prepared using lanthanum hydroxide and chromium
acetate both dissolved in nitric acid stirred 30 and 15 minutes, respectively,
fired at 300°C and of the KERAMAX heating element.

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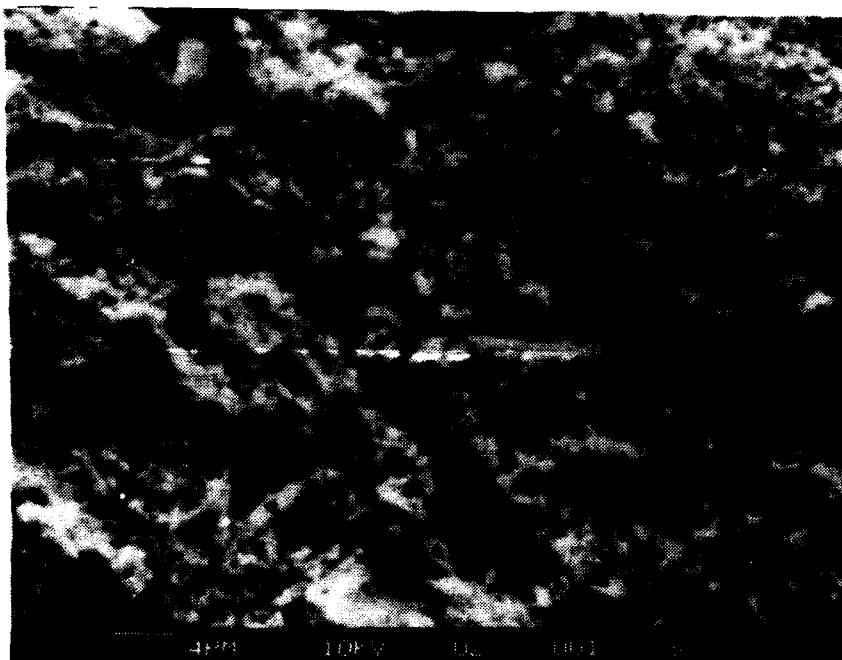
Figure 11. Scanning electron micrograph of the sample (modified Gel #2)
prepared using lanthanum hydroxide and chromium acetate both
dissolved in nitric acid with the hydroxide stirred 30 minutes.
Fired at 300°C.

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concentrations are changed during processing to increase the viscosity. The first step that was taken to increase the viscosity was to eliminate as much water from the solution as possible. Water ligands can stabilize the monomers thus not allowing them to fully condense. A sample, #5, was prepared with ethanol replacing the water in sample #2. The flowchart for sample #5, where the lanthanum hydroxide and chromium acetate were dissolved in 1N Nitric Acid prepared in ethanol is shown in Figure 12. The resulting sample was mostly lanthanum chromite as shown in Figure 13; however the viscosity was not changed significantly and an additional phase crystallized out. Another processing factor that can affect the viscosity of the gel is the pH of the solution.

The next step was to adjust the pH. The pH of sample #2 was approximately 1 due to the presence of the nitric acid. Ammonium hydroxide was used to increase the pH of the solution. (Solution #2 with the addition of NH_4OH is called sample #9.) This procedure is shown as a flowchart in Figure 14. The NH_4OH had three effects. First, the pH was substantially increased with small additions of NH_4OH and NH_3 was liberated. Secondly, the ionic nature of the solution was decreased. Thirdly, the gelation reaction was catalyzed. Enough NH_4OH was added to increase the pH to approximately 7.5. The solution increased its viscosity and seemed to approach gelation exponentially, requiring two days to completely harden. Subsequently, it was found that the rate of gelation is controlled by the pH, ie., the closer to neutral the faster the gelation. Thus by modifying the pH the viscosity range is extended.

The gelled solution was workable (clay-like) and flexible, discontinuous fibers/rods could be formed. Fiber drawing from solution was attempted, however, continuous, uniform fibers could not be drawn from the solution. The fibers/rods formed are shown in Figure 15. These fibers were heat treated and formed polycrystalline lanthanum chromite at 300°C.

Thermogravimetric analysis performed on the fiber is shown in Figure 16. The first and second decreases in weight are identified as the removal of water and acetate, respectively. The third and forth small decreases were unidentifiable. The changes in the structure of the sample at

23
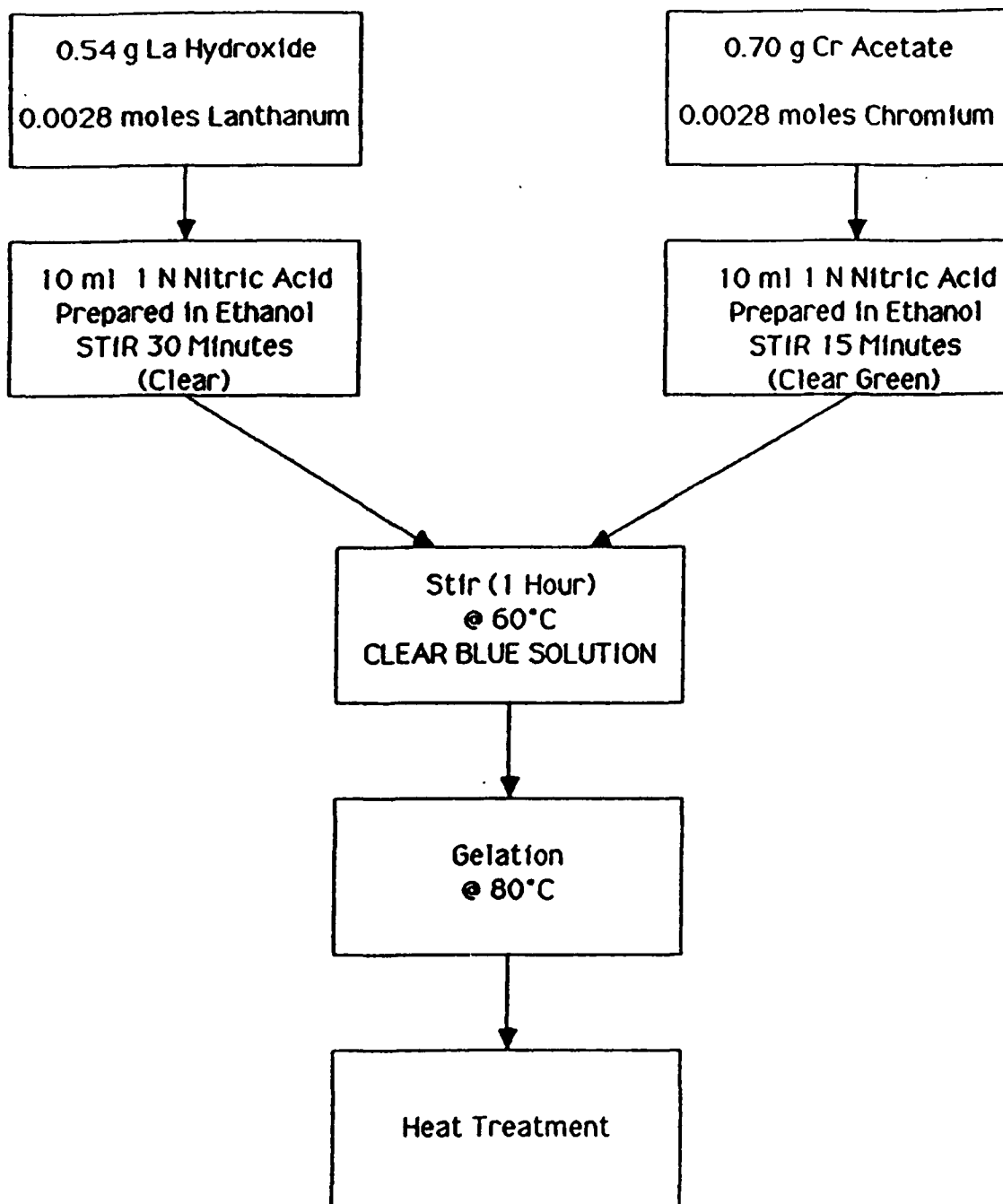
Figure 12. Preparation procedure for lanthanum chromite gel, gel sample #5 (ethanol modified Gel #2) from lanthanum hydroxide in 1 N nitric acid prepared in ethanol and chromium acetate in in 1 N nitric acid prepared in ethanol.

24
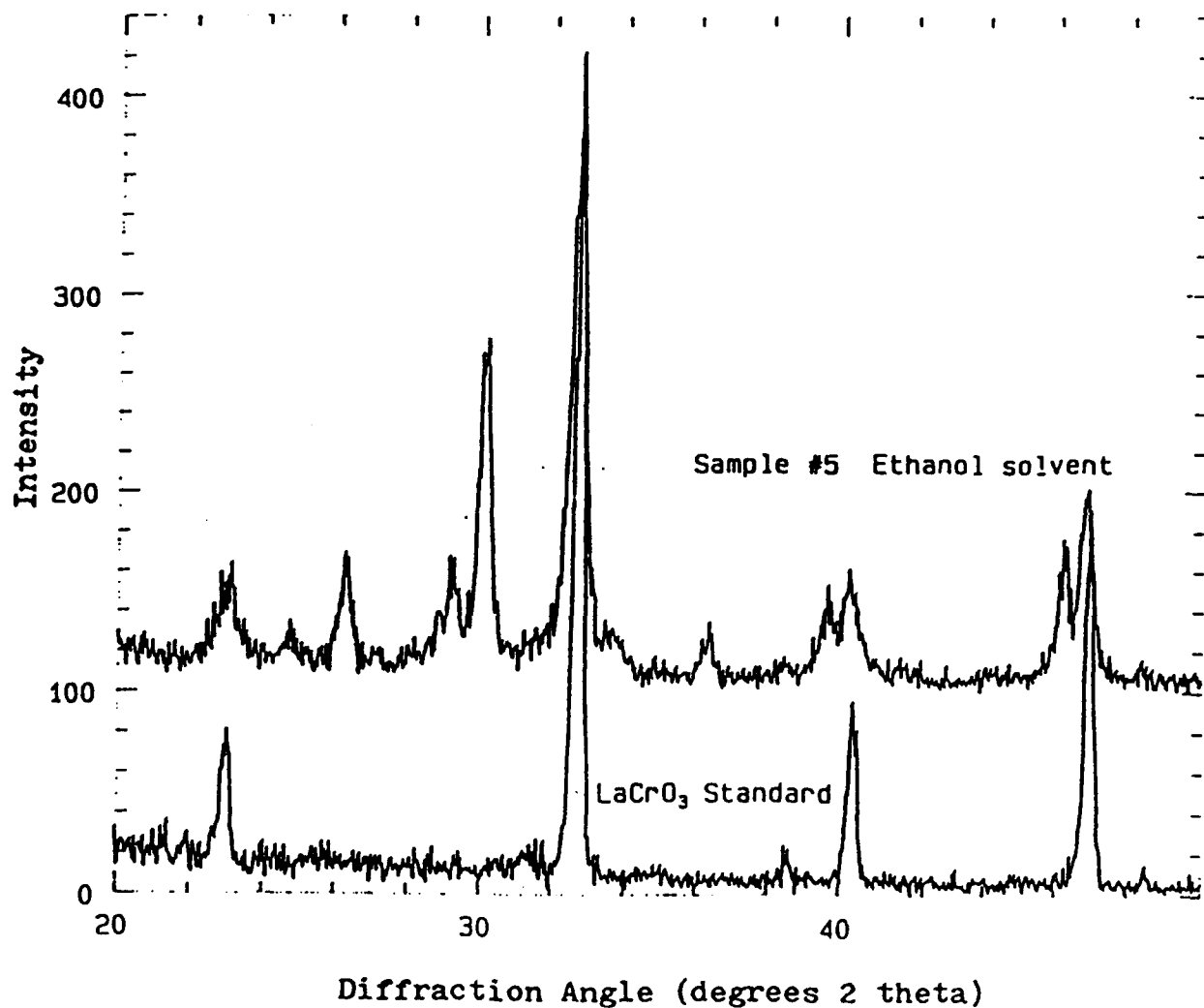
Figure 13. X-Ray diffraction patterns using Cu Kα radiation of the gel sample #5 (ethanol modified Gel #2) prepared using lanthanum hydroxide and chromium acetate both dissolved in nitric acid/ethanol and stirred 15 minutes, fired at 300°C and of the KERAMAX heating element which was used as a standard.

25

```
┌─────────────────────────┐          ┌─────────────────────────┐
│   0.54 g La Hydroxide   │          │    0.70 g Cr Acetate    │
│  (0.0028 moles Lanthanum)│         │  (0.0028 moles Chromium)│
└─────────────────────────┘          └─────────────────────────┘
            │                                     │
            ▼                                     ▼
┌─────────────────────────┐          ┌─────────────────────────┐
│  10 ml 1 N Nitric Acid  │          │  10 ml 1 N Nitric Acid  │
│    STIR 30 Minutes      │          │    STIR 15 Minutes      │
│        (clear)          │          │     (clear green)       │
└─────────────────────────┘          └─────────────────────────┘
              ╲                          ╱
               ╲                        ╱
                ▼                      ▼
          ┌───────────────────────────────┐
          │        STIR ( 1 Hour )        │
          │            @60°C              │
          │     CLEAR BLUE SOLUTION       │
          └───────────────────────────────┘
                          │
                          ▼
          ┌───────────────────────────────┐
          │             ADD               │
          │            NH4OH              │
          │            UNTIL              │
          │           pH~7.5             │
          └───────────────────────────────┘
                          │
                          ▼
          ┌───────────────────────────────┐
          │       GELATION AND            │
          │      FIBER FORMATION          │
          └───────────────────────────────┘
```
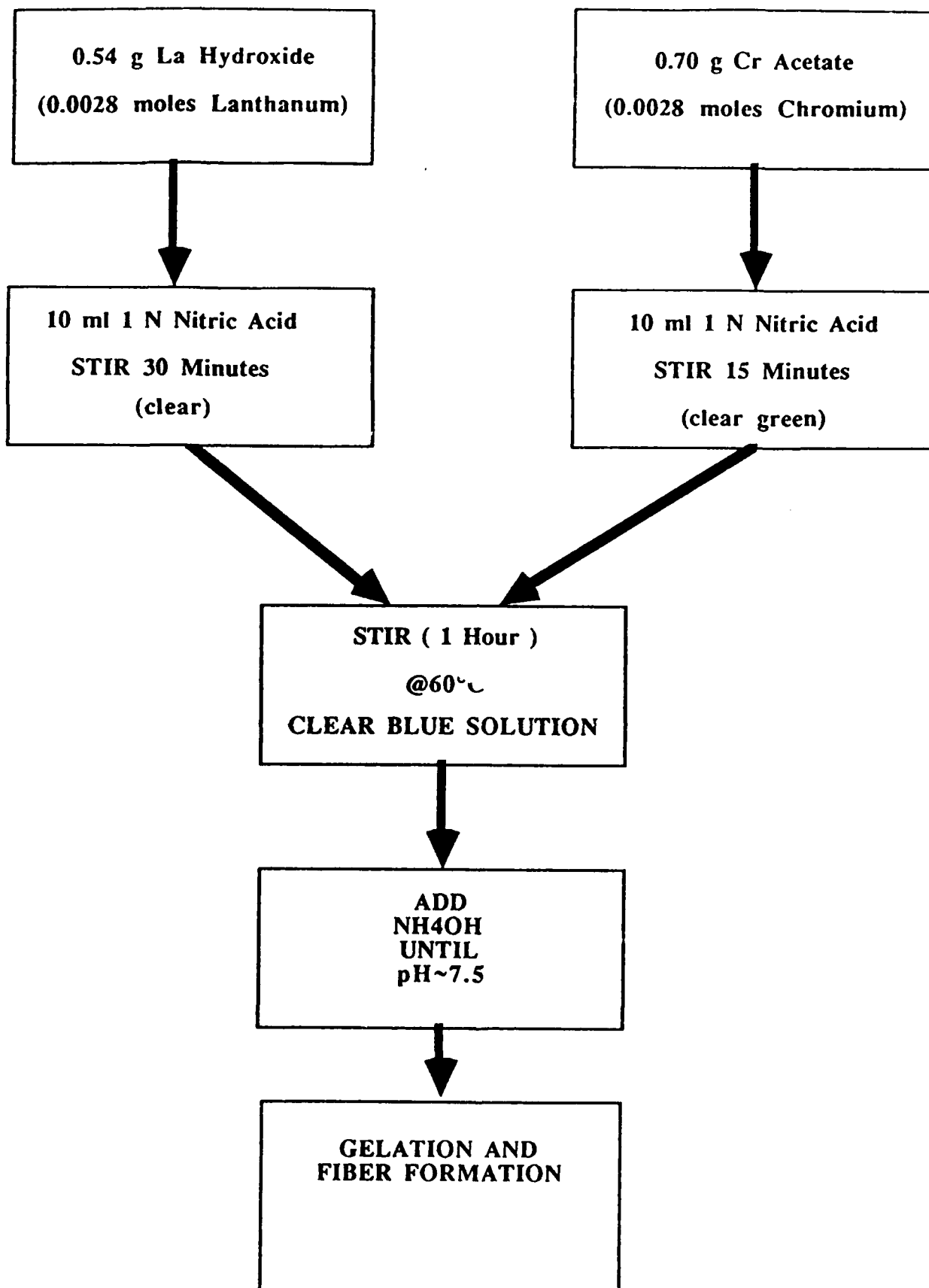
Figure 14.   Preparation procedure for lanthanum chromite gel, Gel #9
(pH modified Gel #2) from lanthanum hydroxide in 1 N nitric acid
and chromium acetate in in 1 N nitric acid. The stirring time before
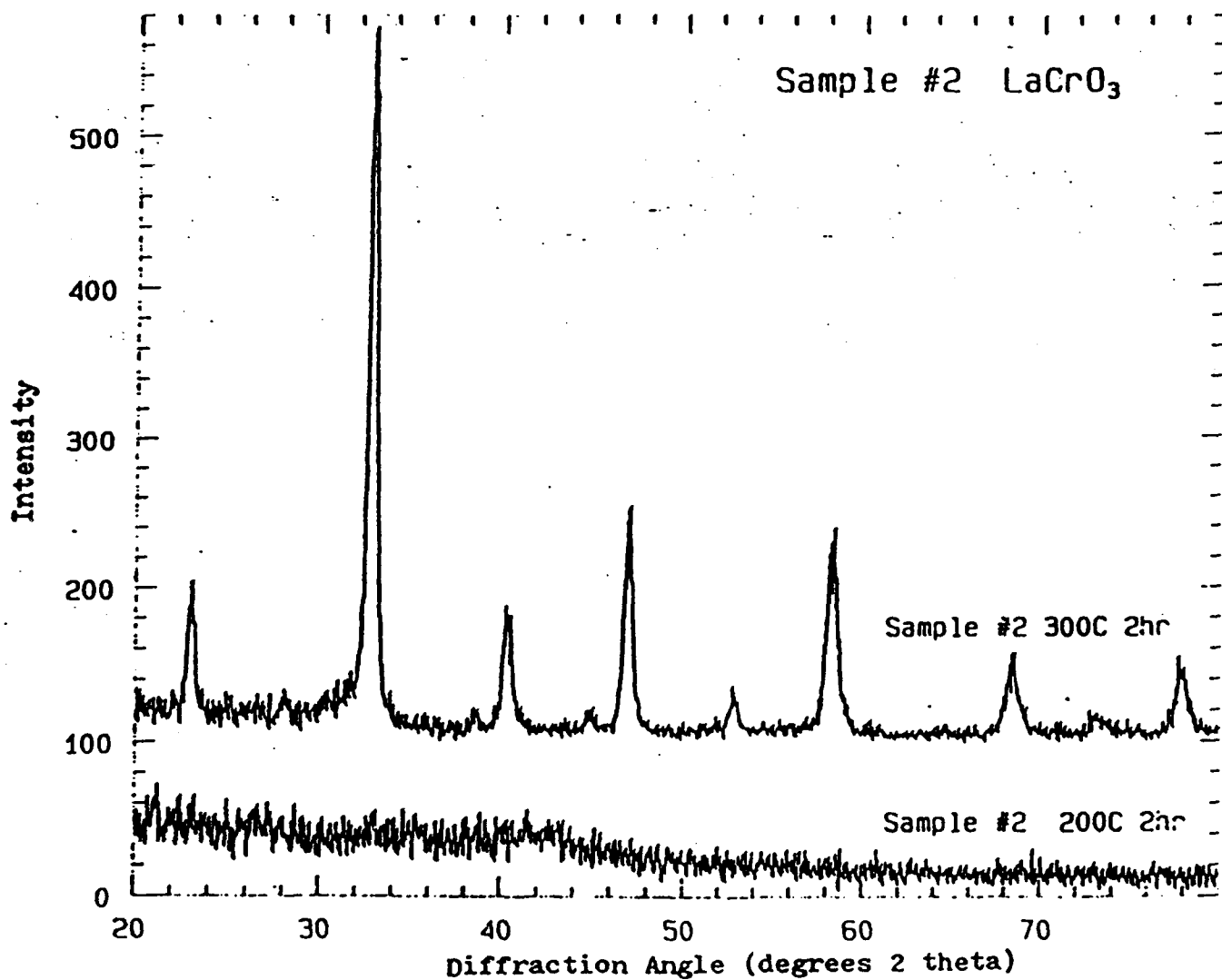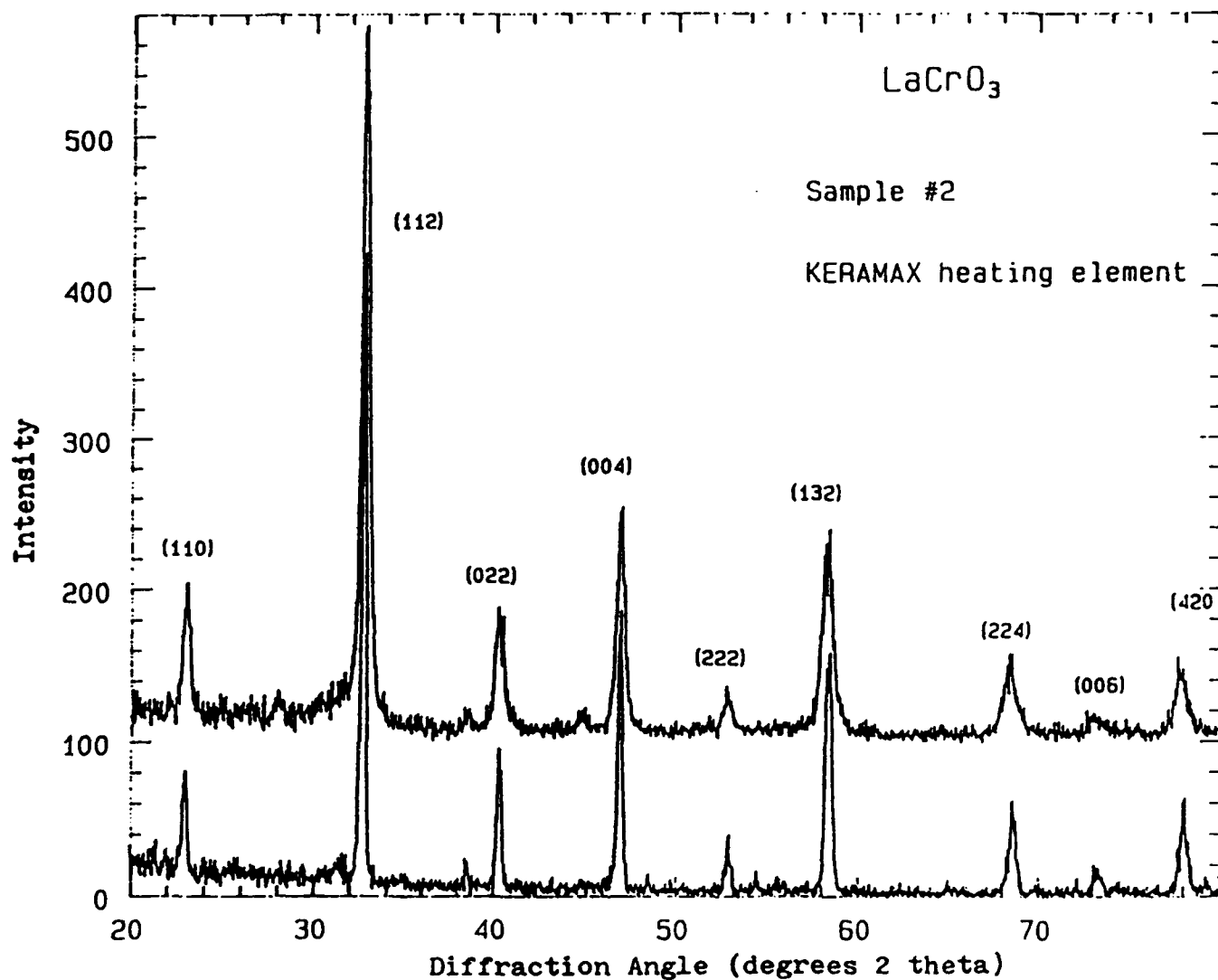mixing was 30 minutes and 15 minutes, respectively. Subsequent
additions of ammonia allowed for controlled gelation.
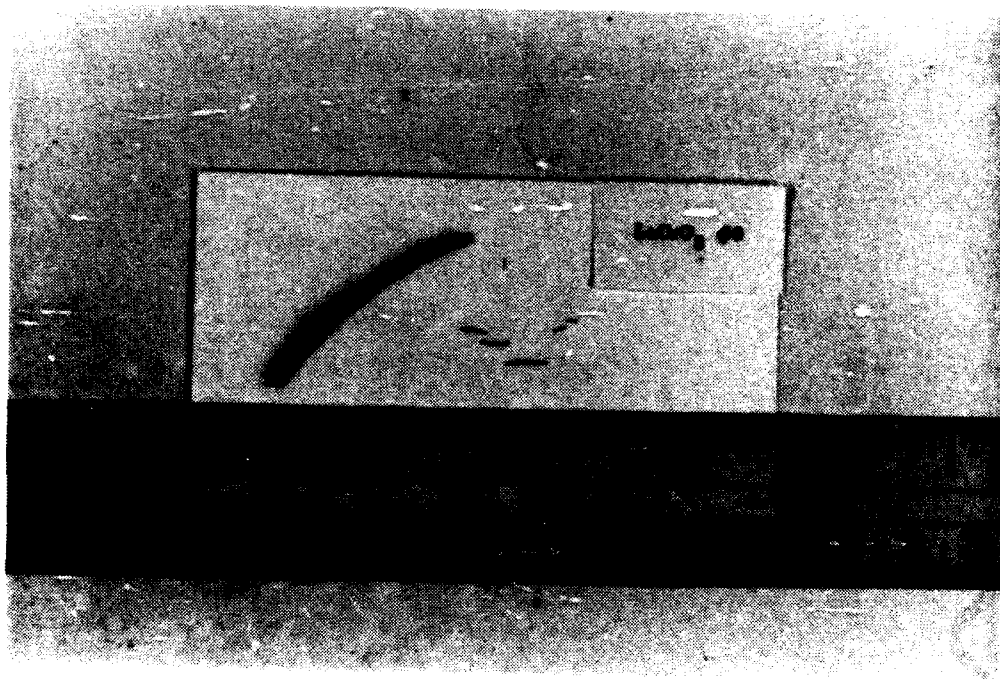
Figure 15. Discontinuous fibers formed from pH modified solution containing
lanthanum hydroxide and chromium acetate in nitric acid, Gel #9.
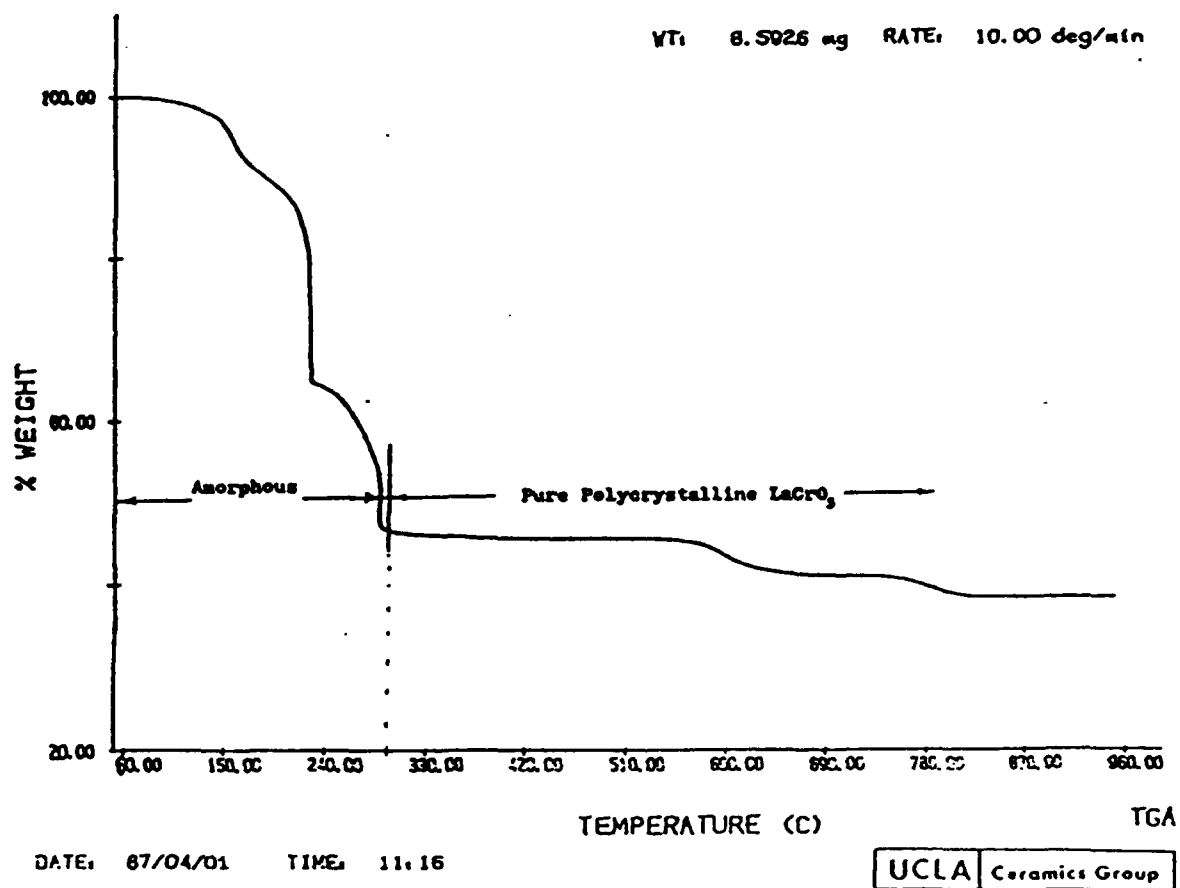
Figure 16. Thermogravimetric analysis of pH modified solution containing
lanthanum hydroxide and chromium acetate in nitric acid, Gel #9.

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different temperatures is indicated on the TGA curve; with the evaporation of acetate the sample becomes single-phase polycrystalline lanthanum chromite. It appears that crystallization can occur only after the organic groups are eliminated. If this is the case then theoretically by modifying the solvents and precursors, the temperature at which lanthanum chromite forms can be changed.

The large weight losses present on the TGA curve demonstrate an inherent problem in sol-gel processing, that of shrinkage. The inability of the sol-gel derived fibers to shrink causes the surface cracks shown in Figure 15. These cracks form due to the evaporation of organics, either from solvents or from the precursors themselves. To minimize the formation of cracks, slow heating and cooling rates were employed. In the case of these small fibers, even very slow heating and cooling rates of 0.2°C/min could not eliminate small cracks from developing on the surface.

Fibers were heat treated in air at 200°C, 230°C and 1000°C for two hours. Subsequent X-ray diffraction showed that at 200°C the sample was amorphous, while at 230°C the sample was pure, crystalline $LaCrO_3$ (Fig. 17). After heat treatment at 1000°C, the diffracted X-ray intensity increased markedly as the lattice became coherent. Also noticeable is the decrease in peak width, reflecting the increase in particle size.

During this phase of the program fibers or rods were obtained; however, these fibers were not drawn directly from the solution. By the above method continuous fiber formation was not achieved. To draw fibers from solution, directional polymerization either of the solvents or of the alkoxides appears to be necessary. In other words the solution must contain some linear polymeric chains. To obtain these chains there must be a polymerizable species. Although the previous samples formed gels, their polycondensation reaction did not result in 2-dimensional chain like growth but in 3-dimensional colloidal growth. One of the more convenient ways to make organic based polymerizable species containing metal - oxygen bonds is by the use of metal alkoxides.[30]
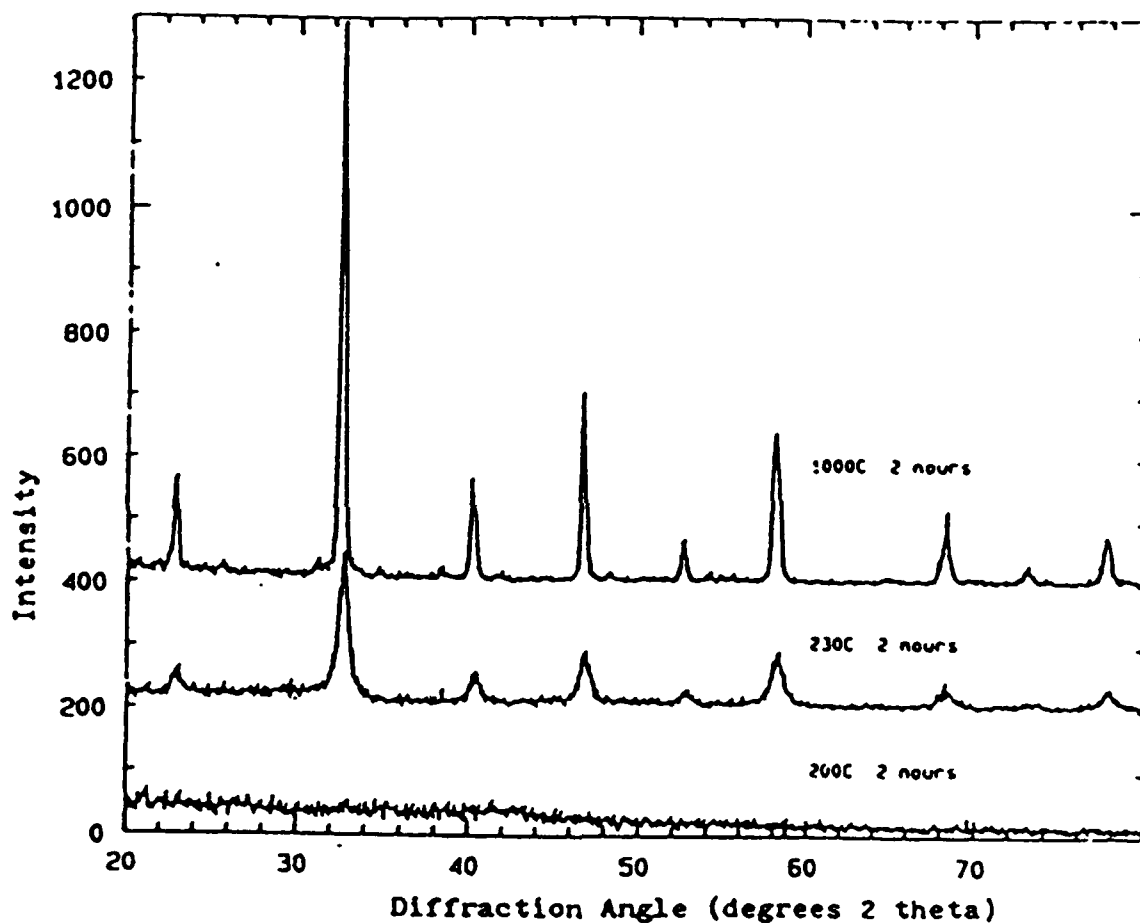
Figure 17. X-ray diffraction of pH modified solution containing lanthanum
hydroxide and chromium acetate in nitric acid, Gel #9, heat treated
at 200°C, 230°C, and 1000°C. The peaks were identified using
JCPDS File # 24-1016.

3.1.3 Preparation of Alkoxides

To utilize alkoxides as precursors for oxide fibers the hydrolysis and polymerization reactions must be controlled. To control the polycondensation reaction an understanding of the hydrolysis and polymerization reactions must be developed. To control these reactions in lanthanum precursors the absence of moisture was imperative. Commercially obtained $La(iOC_3H_7)_3$, for instance, was found to be hydrolyzed and partially polymerized and dissolution in liquid to form sols was difficult.

To reduce the moisture content present in all steps of the process much prudence was required. This included the complete drying of all glassware as well as the distillation of all solvents. In addition all experiments were carried out in dry Argon. This was mandated because both lanthanum chloride, lanthanum metal and lanthanum isopropoxide react with moisture and oxygen. Lanthanum metal in addition reacts with nitrogen. Because of the hydroscopic nature of the lanthanum containing materials an argon dry box was made operational. All material handling was done inside the glovebox except for the distillation and refluxing steps. Two processes to prepare lanthanum isopropoxide were used.

The first process used was that reported by Mazdiyasni in which lanthanum metal is reacted with isopropyl alcohol in the presence of an appropriate catalyst.[31] This reaction is shown below,

$$La \ (metal) + 3i \ C_3H_7OH \rightarrow \ La(iOC_3H_7)_3 \qquad (1)$$

Although this technique resulted in good yields with the lanthanum isopropoxide being soluble in benzene, nonpolymerized lanthanum isopropoxide was not obtained. The reason for this may have been the presence of small amounts of moisture during synthesis.

The second process used to make lanthanum isopropoxide is one that is utilized in the production of other rare earth alkoxides.[32] This process is outlined in Figure 18 and described
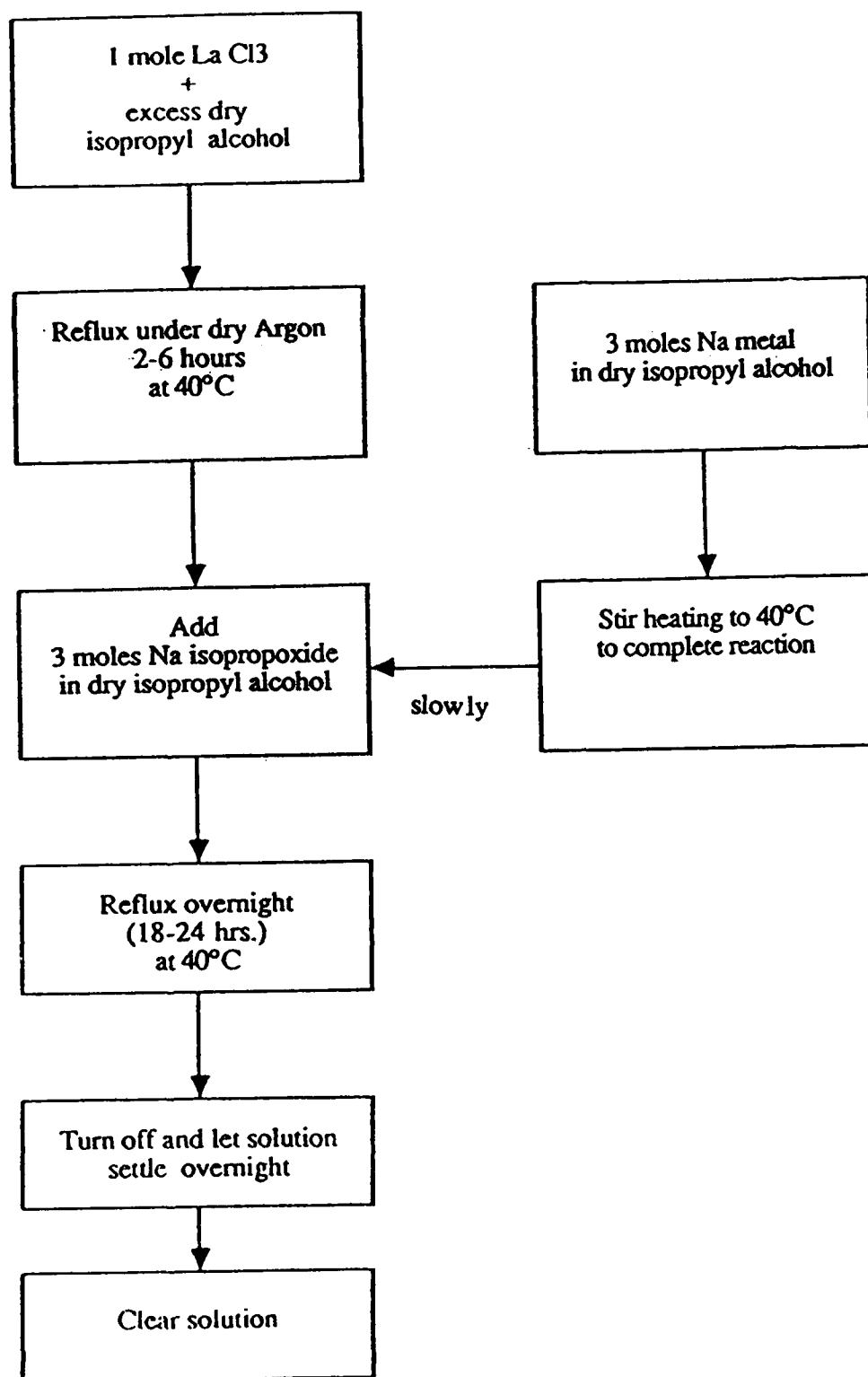
Figure 18. Preparation procedure for lanthanum isopropoxide using LaCl₃.

below. In this procedure lanthanum chloride, $LaCl_3$, is first reacted with excess isopropyl alcohol. An alcoholate is formed, as shown in Equation (2),

$$LaCl_3 + 3i\ C_3H_7OH \rightarrow LaCl_3 \cdot 3i\ C_3H_7OH \qquad (2)$$
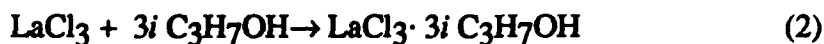
This reaction was carried out by refluxing under Argon from two to six hours at 40°C. The alcoholate forms a colloidal suspension. If the alcoholate is allowed to reflux any longer than this, a clear solution of lanthanum alkoxide is not achievable. A possible reason for this is that polymerization begins to occur between the alcoholate groups. The next step in the process is the addition of sodium isopropoxide. The sodium reacts with the chlorine to form sodium chloride which precipitates out of the solution, leaving lanthanum isopropoxide in solution, as shown in equation 3,

$$LaCl_3 \cdot 3i\ C_3H_7OH + 3Na \cdot i\ C_3H_7OH \rightarrow La(iOC_3H_7)_3 + 3NaCl \qquad (3)$$
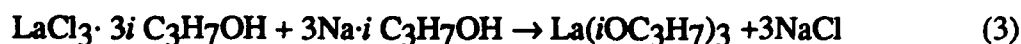
As the sodium isopropoxide is also very hygroscopic, sodium isopropoxide was prepared as needed. In this case, the reactive sodium metal was added to distilled isopropyl alcohol . The metal reacted upon contact; however, heating the solution to 40°C facilitated the reaction. The solution containing the sodium isopropoxide and the lanthanum alcoholate was then refluxed overnight, from 18 to 24 hours at 40°C. The solution was then collected and the NaCl was allowed to settle to the bottom. Within 24 hours of the addition of the sodium isopropoxide the solution became clear. The clear solution was then decanted leaving precipitated NaCl in the reflux chamber. Although the concentration of the lanthanum isopropoxide in the solution was not optimized, the concentration was 6.16 grams lanthanum oxide per 1000 grams of solution. This concentration is high enough to allow for the formation of a lanthanum oxide gel. The concentration can be increased, however with increased concentration the probability of forming unreactive lanthanum complexes is increased.

Characterization of the as prepared lanthanum alkoxide was attempted using infrared spectroscopy. However, the clear solution was too dilute for accurate observation of IR bands due to $La\ (i\ OC_3H_7)_3$. The solution was concentrated and the IR then taken with the

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polymerized solid. The only published infrared spectroscopy data on monomeric lanthanum isopropoxide is shown in Figure 19. This scan was taken as the standard for comparison with the prepared lanthanum alkoxide infrared results. None of the observed infrared bands appear to correspond to those of Figure 19. It is not surprising that the polymerized alkoxide IR bands are very similar to those scans obtained from the lanthanum isopropoxide purchased from Alfa and GFS. Because of the similarity of the IR bands of the prepared alkoxide in the polymerized state to the commercial lanthanum isopropoxide it seems feasible that they are similar chemically.

It should be noted that although the commercially available alkoxide is not soluble in alcohol as purchased, in its original condition it should be soluble. Similarly, the alkoxide prepared at UCLA was soluble when prepared but once concentrated it was not soluble. The IR data of the lanthanum isopropoxide prepared, as well as the purchased lanthanum isopropoxide is shown in Figure 20. The differences between the IR results shown in Figure 19 and Figure 20 are perhaps due to the extent of polymerization.

To obtain a solution capable of controlled viscosity either lanthanum or chromium, should be of the form of a polymerizable organo-metallic such as an alkoxide. As the chromium alkoxides are extremely insoluble in common solvents, lanthanum isopropoxide was produced as discussed above. The way in which the two precursors react with each other or with water controls the solution viscosity.

When mixing the two organo - metallic precursors three of the possible configurations may be obtained, as shown in Figure 21. In the ideal situation a chain containing -La-O-Cr-O-La-O-Cr- chains would be produced, this would lead to the highest degree of homogeneity as seen in (a). However, two other situations can exist which lead to lesser degrees of homogeneity. Although the mixing is at a less intimate, level lanthanum chromite can still be produced. In case (b) and case (c) the problem arises that the individual components may precipitate out leading to macroscopic heterogeneity. If the separate components such as chains of lanthanum and chains

34
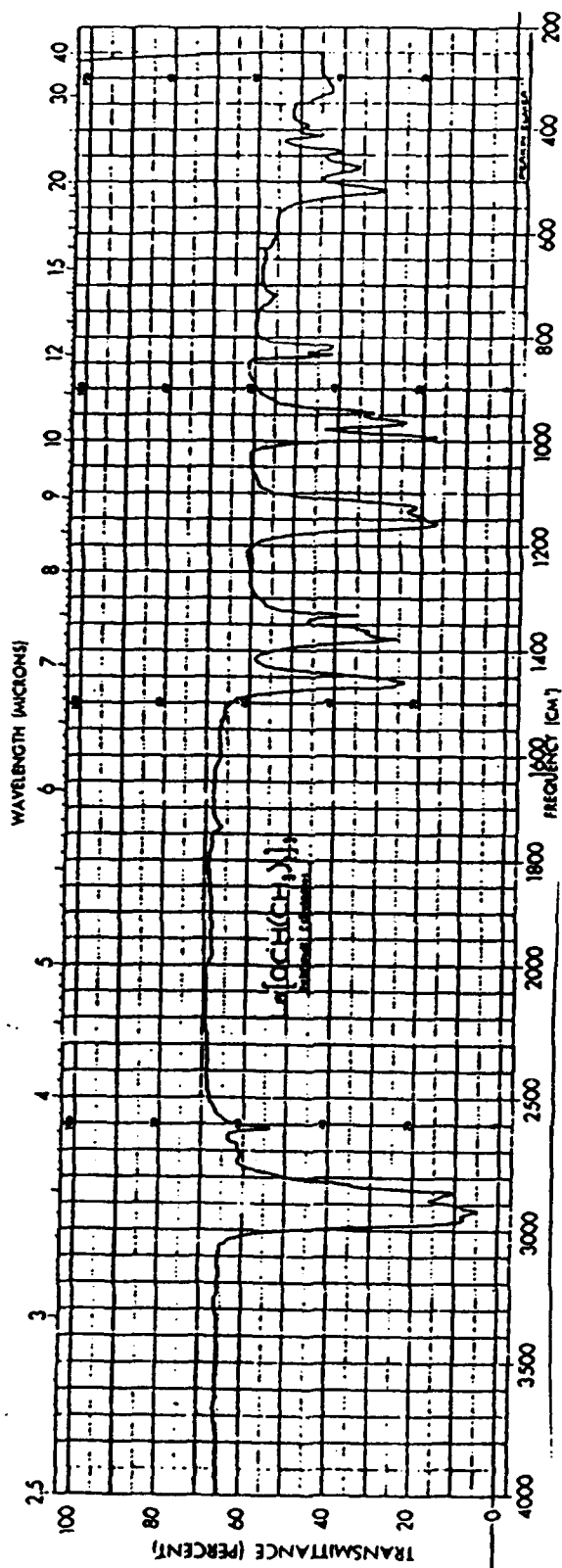
Figure 19. Infrared spectroscopic scan of lanthanum isopropoxide by Mazdiyasni. Obtained from AFWAL/MLLM.

35
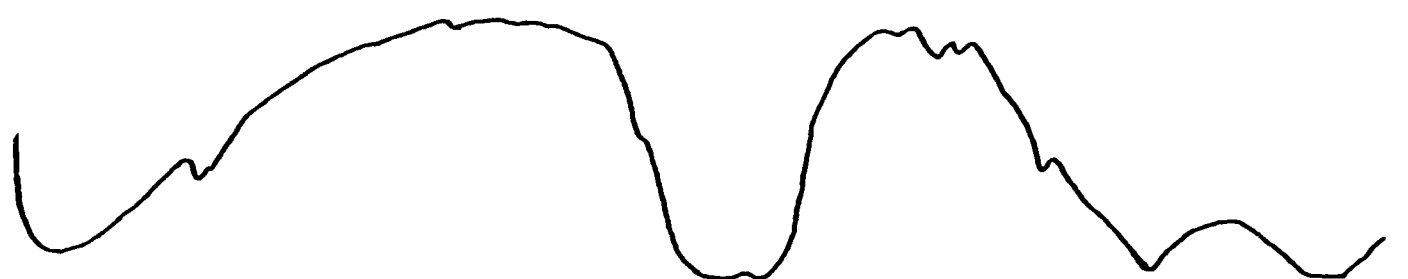
Lanthanum isopropoxide as purchased from GFS Chemicals ↑
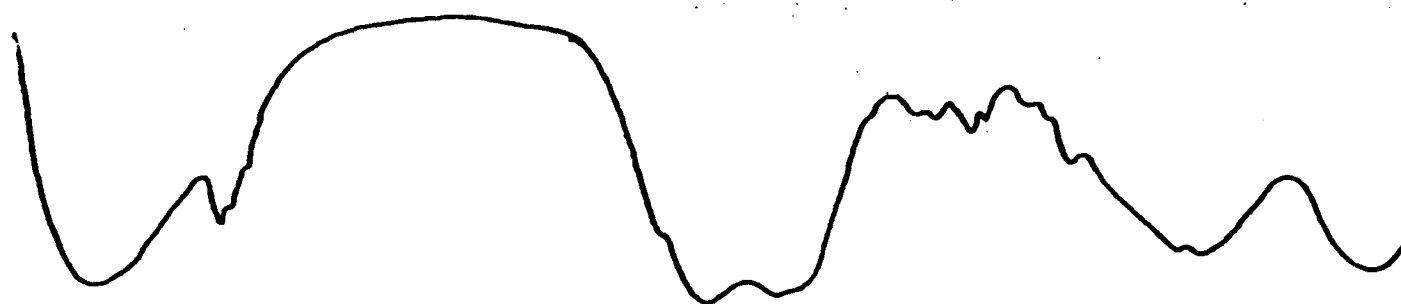
Lanthanum isopropoxide as purchased from Alfa Chemicals ↑

Lanthanum isopropoxide prepared at UCLA ↓

| 3500 | 3000 | 2500 | 2000 | 1800 | 1600 | 1400 | 1200 | 1000 | 800 | 600 | 400 | 200 |
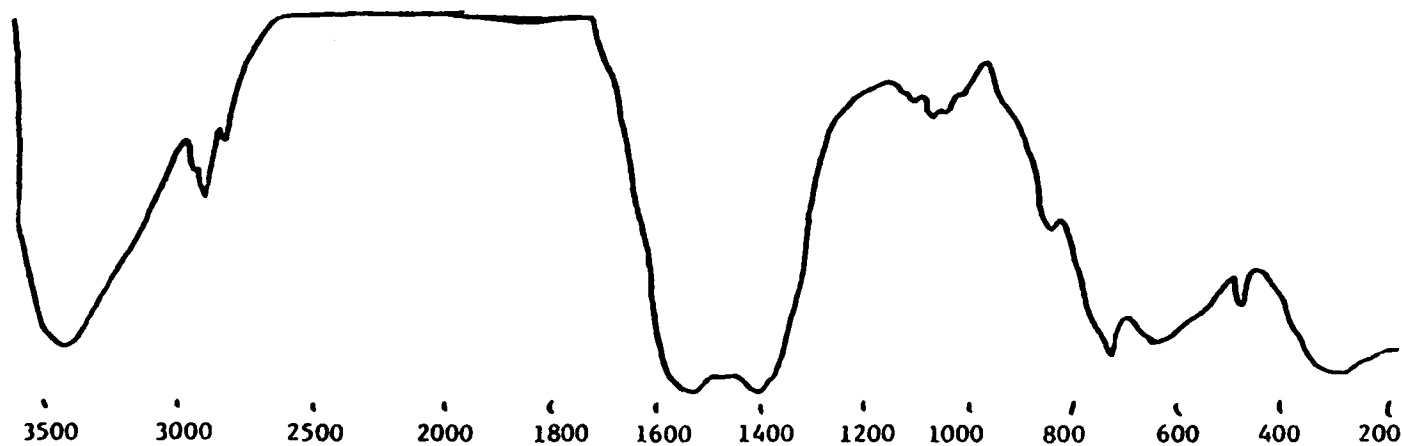
Wavenumber (cm^{-1})

Figure 20. Infrared spectrosopic scans of lanthanum isopropoxide from
three sources, Alfa, GFS, and UCLA.

36
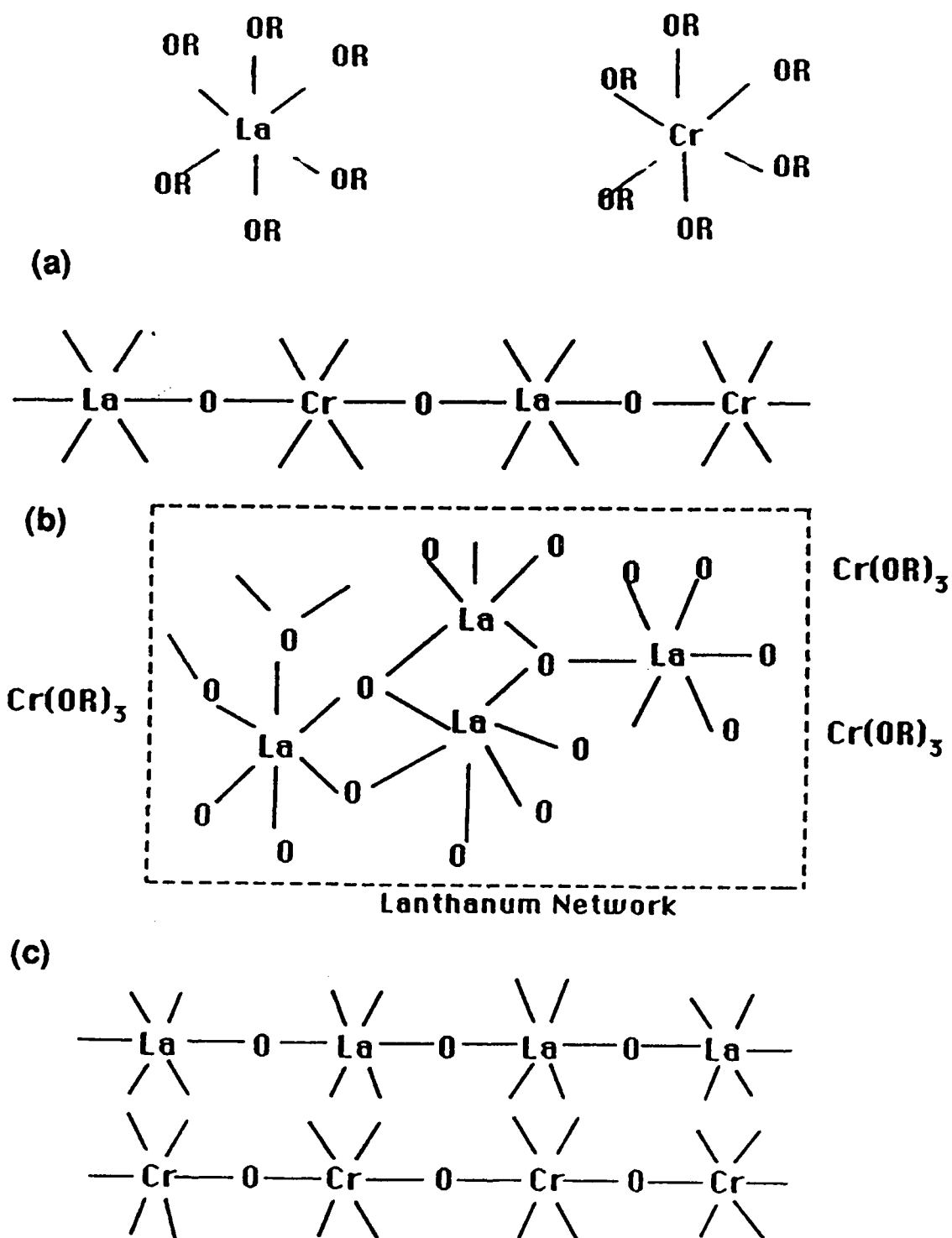
Figure 21. Possible molecular configurations in lanthanum chromite precursor system.

of chromium mix intimately and a fiber or gel can be formed then the lack of molecular level homogeneity can be tolerated.

The next step was to try to produce molecular level mixing of the pre-ceramic precursors. To obtain molecular level mixing, the lanthanum alkoxide was mixed with a variety of chromium precursors. By direct addition, only chromium 2,4-pentanedionate and chromium 2-ethylhexanoate did not produce immediate precipitates. However with these two precursors, the reaction temperature had to be controlled so that precipitates did not form. In the case of the chromium 2,4-pentanedionate the precipitates which form at reaction temperatures less than 50°C appeared to be chromium 2,4-pentanedionate coming out of solution . At temperatures above this the solution gelled before the chromium precipitates formed. The procedure for obtaining lanthanum chromite using chromium pentanedionate is shown in Figure 22.

The second precursor which did not produce instant precipitation was chromium 2-ethylhexanoate. The chromium 2-ethylhexanoate was purchased dissolved in excess ethylhexanoic acid which over time reacted with lanthanum isopropoxide to form an insoluble lanthanum ethylhexanoate. If however the lanthanum isopropoxide was hydrolyzed before an appreciable amount of isopropyl alcohol was exchanged a gel could be obtained which resulted in lanthanum chromite. The procedure for obtaining lanthanum chromite using chromium 2-ethylhexanoate is shown in Figure 23. By controlling the hydrolysis and extent of polymerization the chromium 2-ethylhexanoate solution should allow for fiber formation.

The addition of chromium hydroxide or acetate to the hygroscopic lanthanum isopropoxide led immediately to precipitation, presumably in the form of lanthanum hydroxide. To stabilize the lanthanum isopropoxide the addition of chelating agents was investigated. The addition of one to three moles of ethylhexanoic acid to one mole of lanthanum isopropoxide stabilized the solution without leading to precipitation even upon exposure to air. At temperatures less than approximately 50°C, however, lanthanum ethylhexanoate formed and precipitated out. Thus if the proper amount of ethylhexanoic acid is added, precursor containing hydroxide groups should
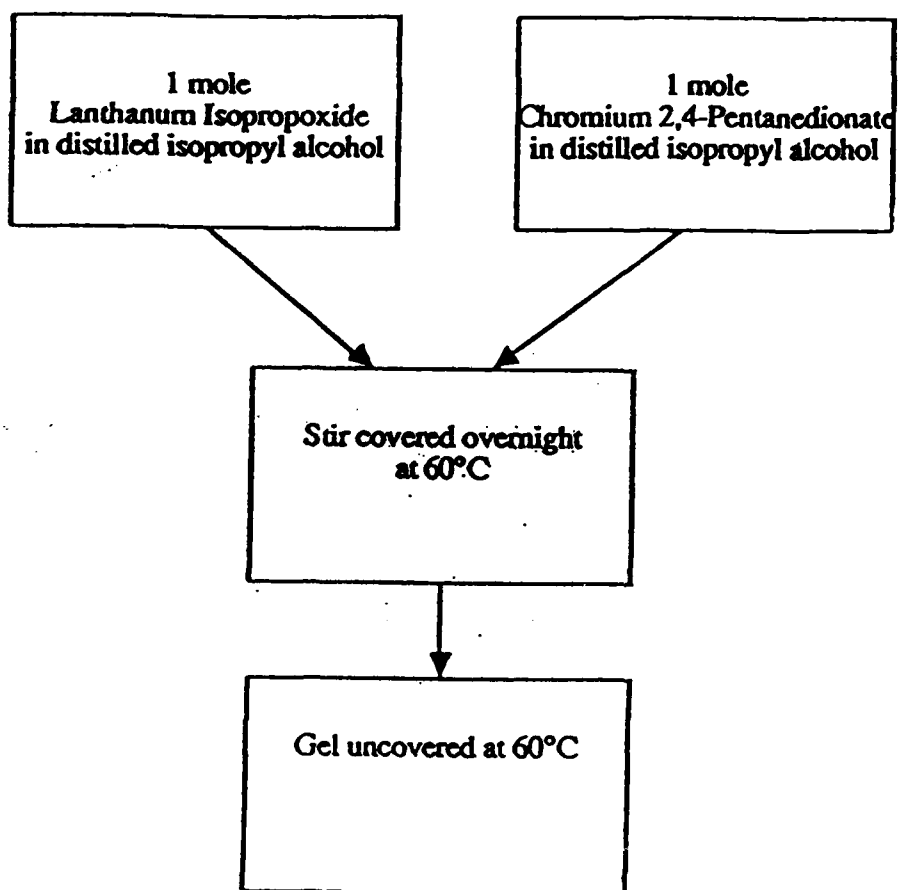
Figure 22. Preparation procedure of lanthanum chromite using lanthanum
isopropoxide and chromium pentanedionate.
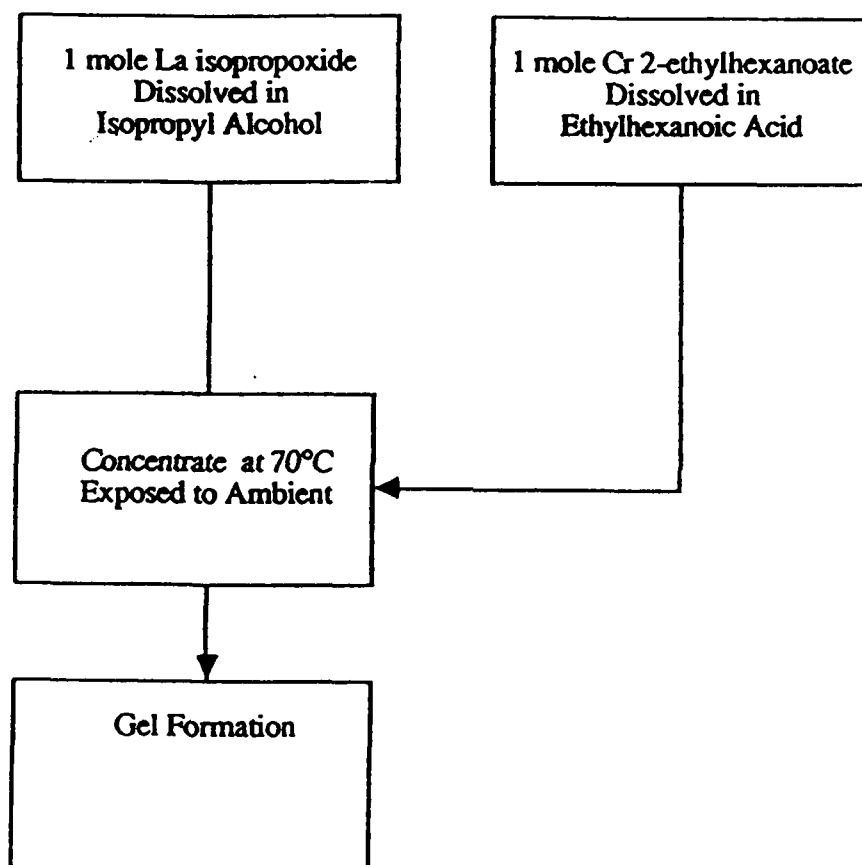
Figure 23. Preparation procedure using lanthanum isopropoxide and chromium 2-ethylhexanoate.

not yield lanthanum hydroxide. This method of prestabilizing certain alkoxides has been used at UCLA for the preparation of $PbZrTiO_3$ fibers and was investigated for the preparation of lanthanum chromite fibers, however inconclusive results were obtained.

3.1.4 Fiber preparation

The lanthanum chromite fiber preparation procedure was modified from the procedure shown in Figure 23. However the exact time at which concentration occurs and the exact concentrations of the precursors appears to greatly effect the fiberizability of the solution. This may be due to the fact that if the extent of hydrolysis is too great or the extent of chelation is too great than a precipitate will occur. Complete chelation or hydrolysis is not detrimental in all cases, however, in the case of lanthanum, both lanthanum ethylhexanoic acid and lanthanum hydroxide precipitate. The optimum condition for fiberization appears to be a partially hydrolyzed and partially chelated precursor. This would then allow for polymerization to occur in a linear array.

A photograph of an as drawn fiber is shown in Figure 24. These fibers retain their shape upon firing but are extremely fragile due to their porosity. This porosity can be seen in the scanning electron micrograph of the cross section shown in Figure 25. Figure 26 shows the as drawn surface fired to 900°C and held for six hours. It is also obvious in the as drawn surface that the porosity is significant.

To understand how the densification and crystallization occurs, the crystallization kinetics must be investigated. Using differential scanning calorimetry a preliminary time, temperature and transformation (TTT) curve was obtained. The TTT curve is shown in Figure 27. The crystallization began at 370°C. This may be related to the point where a significant amount of the organics are gone which in turn allows for shrinkage and thus crystallization.

At present the method used to produce fibers is to draw them by hand from a viscous solution. The hygroscopic nature of the precursors allows for the complete gelation of the fibers

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LaCrO$_3$ Ceramic Precursor

Fibers As Drawn

3 inches
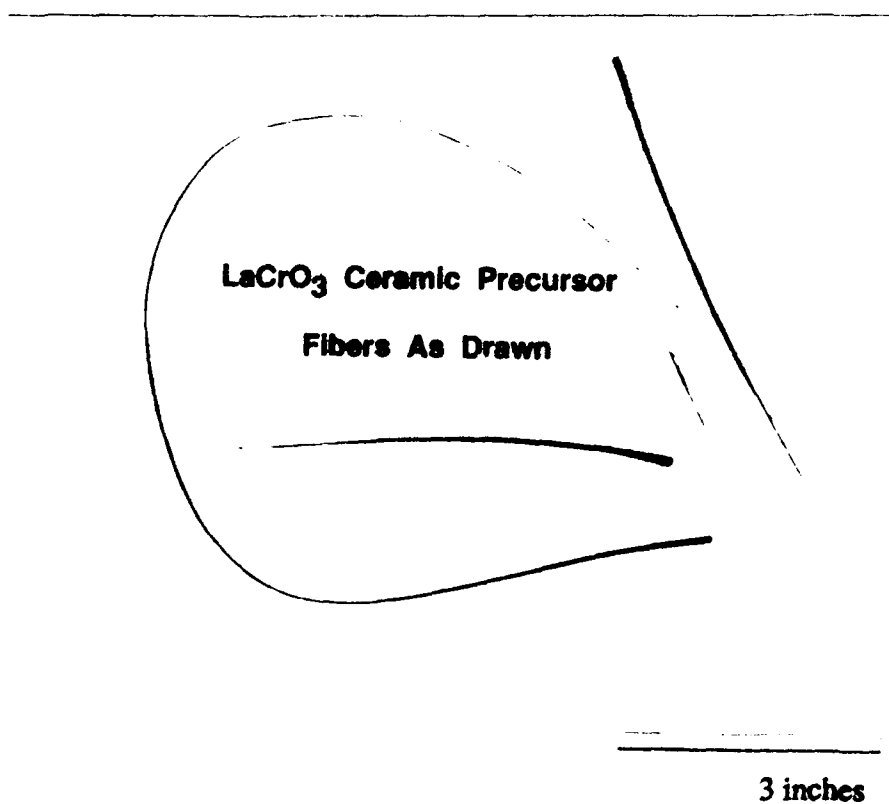
Figure 24.   Photograph of the as drawn fibers drawn from a concentrated
            lanthanum isopropoxide and chromium 2-ethylhexanoate.

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Figure 25. Scanning electron micrograph of the fracture surface of the fiber
prepared from lanthanum isopropoxide and chromium 2-ethylhexanoate.

43
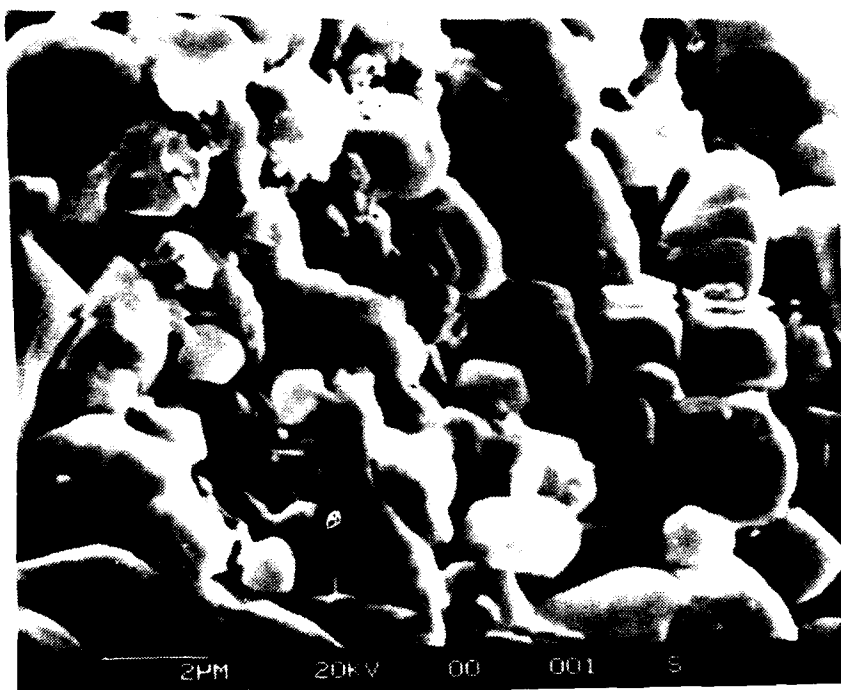
Figure 26. Scanning electron micrograph of the drawn surface prepared from lanthanum isopropoxide and chromium 2-ethylhexanoate fired at 900°C for 6 hours.

44
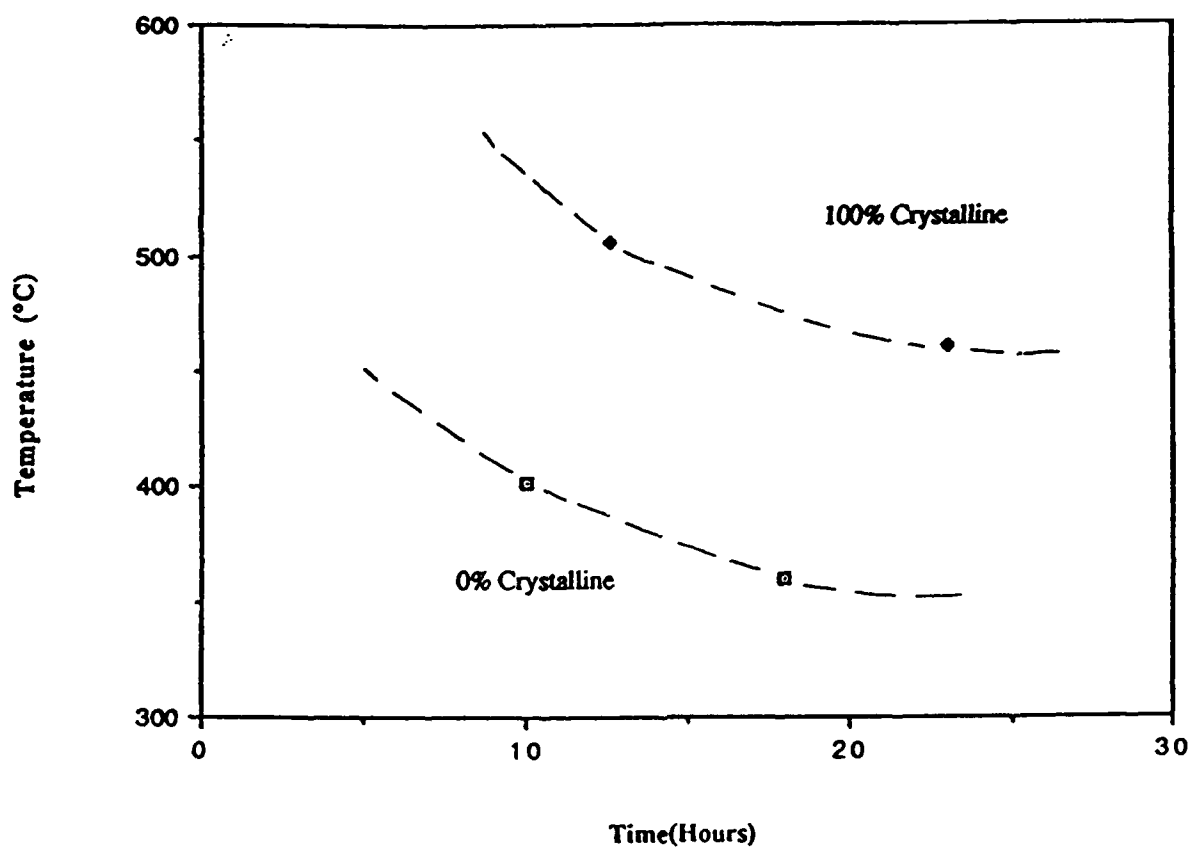
Figure 27. Preliminary Time-Temperature-Transformation curve for sample
prepared from lanthanum isopropoxide and chromium
2-ethylhexanoate.

from the atmospheric moisture. However this method can not be used to produce long fibers with constant diameters. To prepare long, continuous fibers a fiber drawing apparatus was designed. The fiber drawing apparatus consists of three regions, the pressure vessel, the curing zone and the take up wheel. By introducing steam to the as drawn fiber the fiber structure becomes more crosslinked and thus could be wound on the take up spool, without a long aging time. The fiber drawing apparatus is shown in Figure 28.

3.2   Feasibility of Lanthanum Chromite in High Temperature Applications

In addition to preparing lanthanum chromite, one of the purposes of this program was to assess the applicability of lanthanum chromite fibers as reinforcement fibers in high temperature oxidation resistant composites. The following steps were chosen to assess whether lanthanum chromite fibers could be used in composite applications. First, the materials requirements of a composite containing lanthanum chromite were addressed. The composites could utilize matrices which would enhance the stability of the lanthanum chromite. Second, the commercial heating element was characterized. By understanding the use of lanthanum chromite as a heating element it was hoped that insight could be gained into the feasability of lanthanum chromite fibers in high temperature composite applications. The design of the element was understood. Third, the weight loss of the heating element in an oxidizing atmosphere was measured. An attempt to minimize the weight loss was made by coating the samples with an oxygen barrier, ie. alumina.

3.2.1   Stability of Lanthanum Chromite for Composite Applications

The potential application of the lanthanum chromite fibers developed in this program will be as fibers for high temperature composites. The materials parameters, like thermal stability, matrix-fiber solid state reactions, and mechanical strength, necessary in high temperature oxidation resistant composites should be examined. The stability of lanthanum chromite thus must be addressed with respect to these parameters.

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Part 1: Solution reservoir with syringe in pressure chamber

Control of - Atmsophere Nitrogen/Argon
- Temperature : 2 zones T1, T2
- Pressure

Exhaust

Glass

T1

T2

Aluminum

Argon/Nitrogen

Metallic Rings

Part 2: Curing Zone

3 Metallic Rings inside glass tube

T3

Controll of - Temperature T>100°C
- Atmosphere
Argon/Water Vapor

Water Vapor

Argon

Part 3: Take up spool
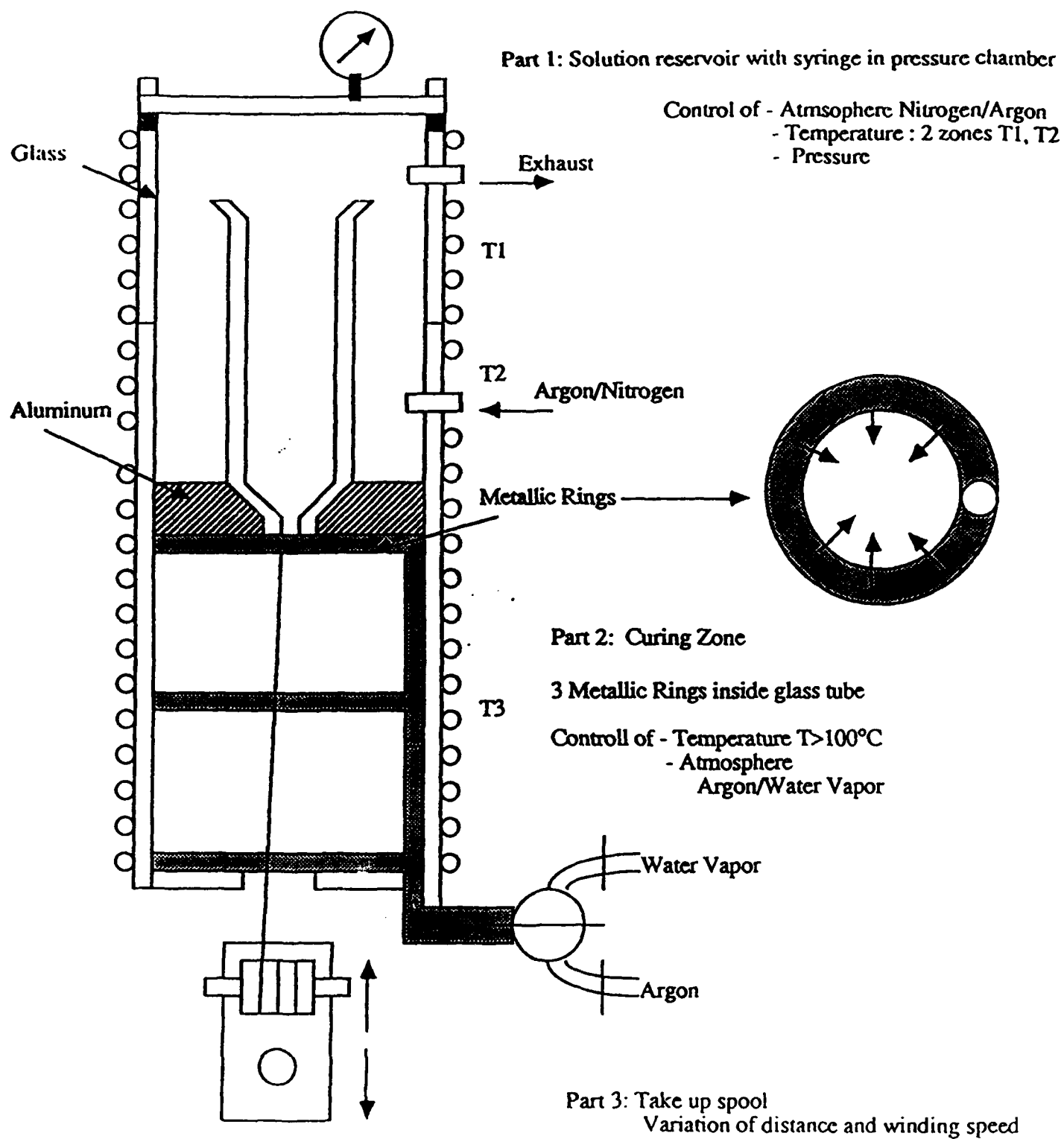Variation of distance and winding speed

Figure 28.   Fiber production apparatus.

An ideal composite contains both an oxidation resistant matrix and oxidation resistant fibers. In the ideal case the fiber provides the mechanical strength. The matrix does not have to be dense to provide oxidation resistance, but only to enhance the mechanical strength. Additionally, the matrix and composite should not react with one another.

In a less ideal but still viable situation the composite contains an oxidation resistant matrix and thermally stable fibers. In this less than ideal case the fibers provide mechanical strength and not oxidation resistance; however, the matrix in this case must be dense to inhibit the gaseous transport to and from the oxidizable fibers which may lead to degradation. In either case, the thermal stability of the fibers must be known in order to select a compatible high temperature composite for lanthanum chromite fibers.

3.2.2 Characterization

Lanthanum chromite, $LaCrO_3$, heating elements are made by FUJI SHO for their KERAMAX line of electric furnaces. The KERAMAX furnace can reach 1800°C in three hours. A variety of size heating elements which range in size from 1.4 cm in diameter to 1.8 cm in diameter with lengths from 18 cm to 55 cm are produced. In order to understand how the heating element is made and why it can withstand such temperatures, an element was purchased from LeMont Scientific. The element that was purchased is shown in Figure 29. It was in the form of a thick walled hollow tube. The element was dissected for electron microscopy and X-ray analysis. A sample was also sent to Coors Spectrochemical Laboratory in Boulder, CO for chemical analysis.

The element consisted of a $La_{1-x}Ca_xCrO_3$ tube attached to silver electrodes. The inside of the tube was packed with Cr_2O_3 grains. The chemical composition was found to vary from the middle to the end sections. In the end sections x = 0.0853 and in the middle section x = 0.0038. Although the calcium ($r_{Ca^{2+}}$ =1.00 A°) substitutionally replaced lanthanum ($r_{La^{3+}}$ =1.06 A°) the X-ray pattern did not change indicating that the Ca caused neglible strain in the lattice. The calcium was added to modify the resistance in the heating element, by changing the carrier
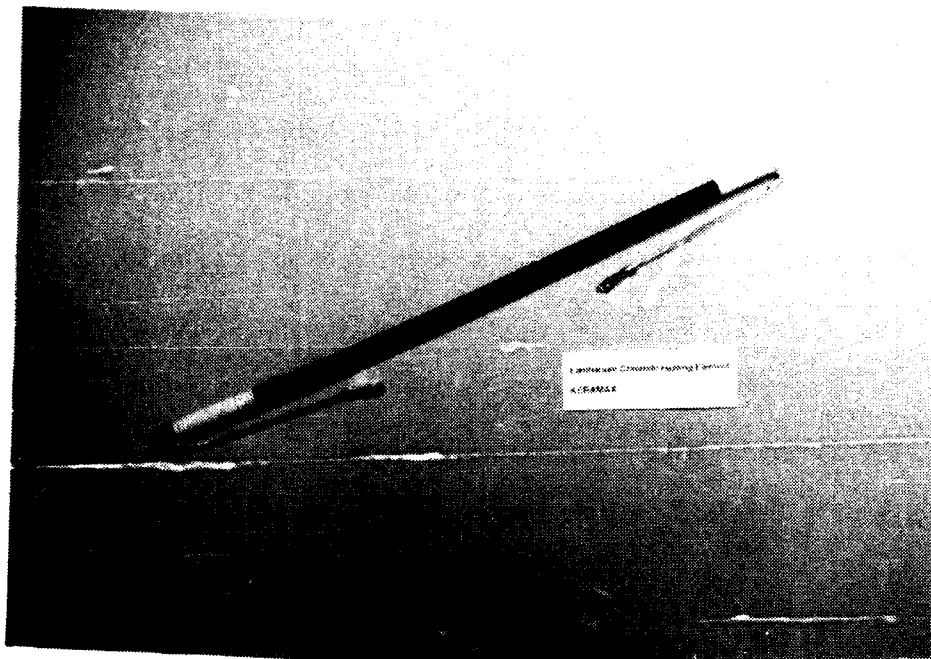
LeMont Scientific

2011 Pine Hall Drive

Science Park

State College, PA 16801

(814)238-8403

Figure 29.   Lanthanum chromite heating element purchased.

concentration. The chromia grains packed into the center of the element were identified through chemical analysis and energy dispersive spectroscopy, the exact oxygen content was not determined. The X-ray pattern showed Cr_2O_3 and an unidentifiable phase with slightly different lattice parameters. It is possible that the pattern relates to a chromium deficient or oxygen rich chromium oxide as the EDX showed only chromium in the powder.

The bulk density, apparent density and the porosity of the end and middle sections are shown in Table 6. The middle section was less porous than the end sections. The young's modulus and the resistivity of the end section are also listed in Table 6. The young's modulus, 14.2×10^6 psi, is reasonable for a nonstructural ceramic with a porosity of 27 percent.

The grain size was approximately 7 microns in the end sections. Figure 30 shows an SEM micrograph at 2000x. The sample was polished and etched to enhance the structure. The micrograph clearly shows the sintered grains, presumably obtained from hot pressing. FUJI SHO has several Japanese patents which describe the development of the lanthanum chromite heating element, as well as the electrical furnace design. The Japanese patents related to lanthanum chromite have been translated.

3.2.3 Thermal Stability in Oxidizing Atmospheres

Although it was known that at very high temperatures, ie. 1700°C, $LaCrO_3$ loses weight through the vaporization of chromium oxide, at the beginning of this program chromium vaporization was not considered to be a serious problem because of the success of a Japanese $LaCrO_3$ heating element guaranteed for extended use at 1800°C. Analysis of the heating element showed that Cr_2O_3 powder was contained inside the hollow $LaCrO_3$ heating element, presumably, to minimize weight loss at high temperatures. The exact mechanisms of the loss and the replenishment of the chromium oxide in the heating element are not known. By engineering the solution to the chromia vaporization, the Japanese were able to guarantee the use of their element for 200 hours at 1800°C.

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Table 6 Physical properties of the heating element.

Young's Modulus and Poissoin's Ratio

$$E = 14.21 \times 10^6 \text{ psi}$$

$$s = 0.17$$

Measured By Pulse Echo Method Where

$$E = (3v_s{}^2(v_l{}^2 - 4/3v_s{}^2)x$$

$$\text{apparent density})/(v_l{}^2 - v_s{}^2)$$

$$s = (v_l{}^2 - 2v_s{}^2)/(2(v_l{}^2 - v_s))$$

Standard Material-Aluminum

$$E_{Reported} = 10 \times 10^6 \text{ psi}$$

$$E_{Measured} = 10.04 \times 10^6 \text{ psi}$$

$$s = 0.33$$

Resitivity

$$r = 150.33 \text{ ohm-cm}$$

Chemical Analysis

$$La_{1-x}Ca_xCrO_3 \quad X_{end\ section} = 0.0853*$$

$$X_{middle\ section} = 0.0038*$$

$$Cr_2O_3 \qquad <50ppm\ Ca*$$

EDX and X-Ray showed only $LaCrO_3$ with very little peak shifts , one peak had shifted 0.02 degrees. EDX of the Cr_2O_3 showed only Cr; X-Ray however showed two or more phases, with similar lattice parameters.

* Done by Coors Analytic Laboratory in Golden, CO.

Bulk density, apparent density, and porosity of the end and middle sections of the heating element by Archimedes method.

Sample	Bulk Density (g/cc)	Apparent Density (g/cc)	Percent Porosity (%)
End Sample (High Ca)	4.72	6.48	27.1
Middle Sample (Low Ca)	5.64	6.39	11.8

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Figure 30. Scanning electron micrograph of the end section of the
lanthanum chromite heating element.

The thermal stability of lanthanum chromite was investigated by heating lanthanum chromite samples obtained from fragments of the Japanese heating element, in air at 1600°C and then weighing the sample. Figure 31 shows the weight loss percent versus time for a sample initially weighing 2.2552 grams with an approximate surface area of 0.9 in^2. It should be noted that these sections from the Japanese heating element were only 88.2 percent dense. Japanese work[33] had demonstrated that the LaCrO$_3$ heating element could be buried in Al$_2$O$_3$ powder with no apparent reaction. Theoretically, the LaCrO$_3$ fibers might be dip coated with an Al$_2$O$_3$ coating to minimize vaporization losses. By dip coating the lanthanum chromite with alumina the thermal stability should be enhanced. The Al$_2$O$_3$ coating can be applied by the sol-gel method as previously demonstrated[34].

To minimize the weight loss of the lanthanum chromite, the samples were coated with alumina. Figure 32 shows the process used for coating the lanthanum chromite with aluminum di(sec butoxide) acetoacetic ester chelate. This has been shown to produce dense alumina films on glass substrates at temperatures as low as 600°C.

Lanthanum chromite pieces with surface areas of approximately 2 in^2 were dip-coated with the above solution. The samples were weighed after a 600°C heat treatment and again after 1100°C heat treatment. The weight change was insignificant, however the higher temperature heat treatments assured that the alumina film contained no organics. Weight loss experiments of the coated and uncoated samples were conducted, by weighing the sample before and after firing. A bottom loading furnace was used so the sample could be at temperature for a specific amount of time. The weight loss of the coated and uncoated samples at 1500°C and 1600°C are shown in Figure 33 and Figure 34. The coating significantly decreased both the rate of vaporization and the quantity of material lost. It is interesting to note that in a plot of percent weight loss versus the square root of time the relationship is linear. This implies a diffusion controlled process as described by Fick's law, further studies would be needed to determine whether the process is cation or oxygen controlled. The slope or rate of loss also changes significantly between the
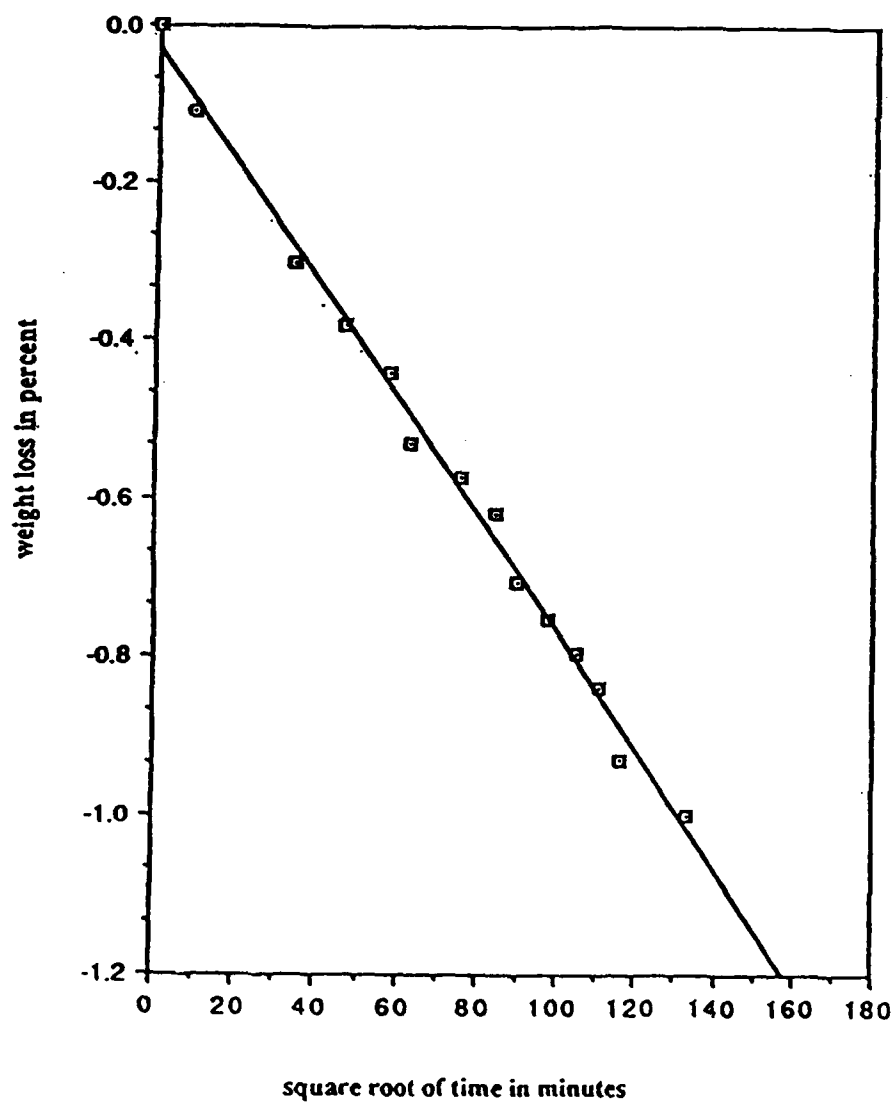
Figure 31.   Weight loss of lanthanum chromite in air at 1600°C.
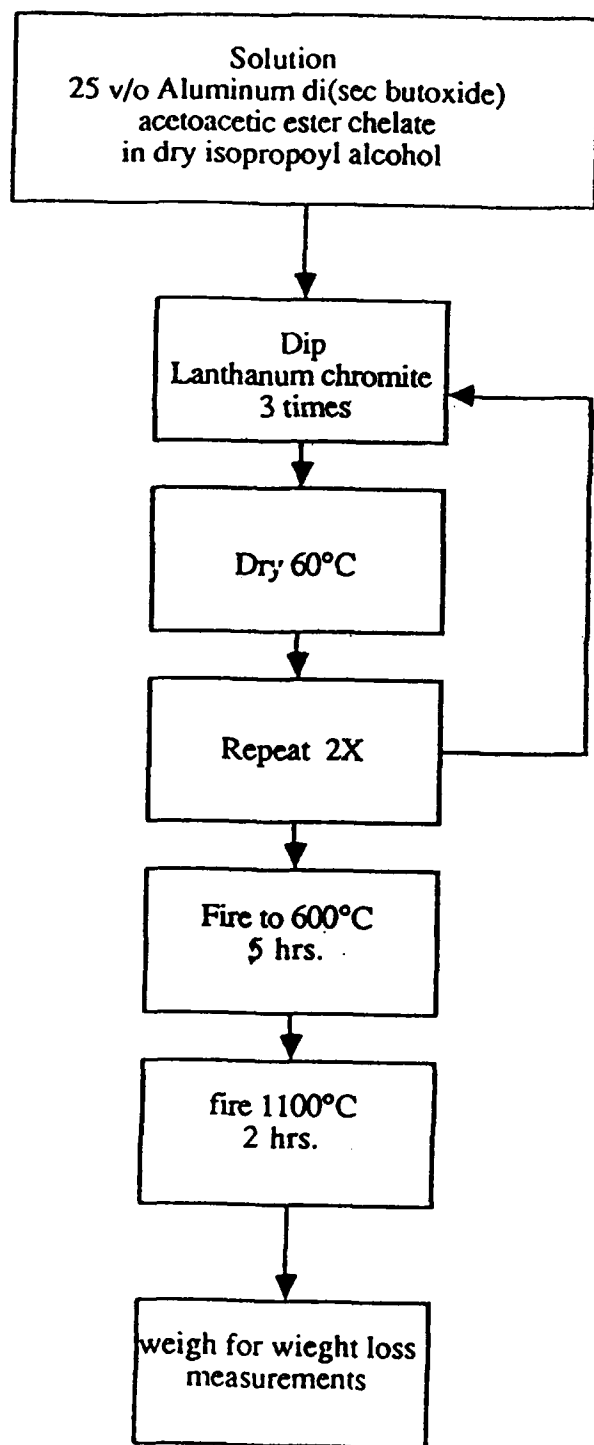
Figure 32. Process of coating lanthanum chromite with alumina.
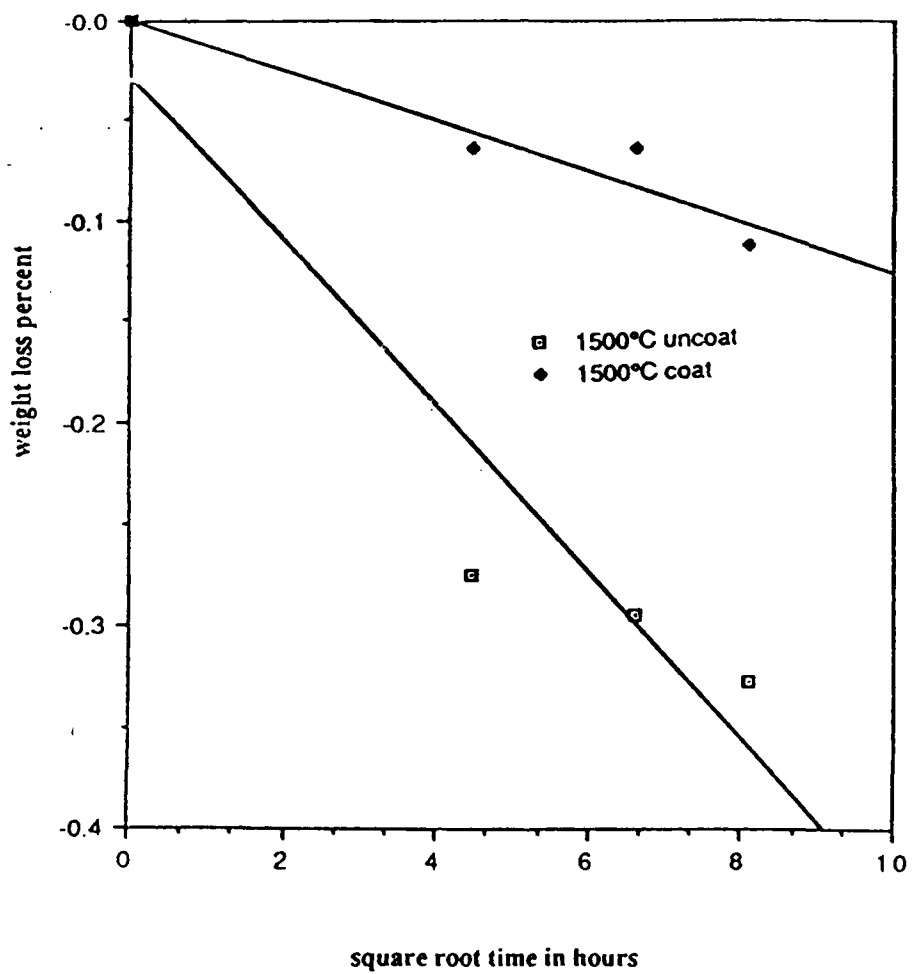
Figure 33. Weight loss of coated and uncoated lanthanum chromite heating element at 1500°C versus square root of time.
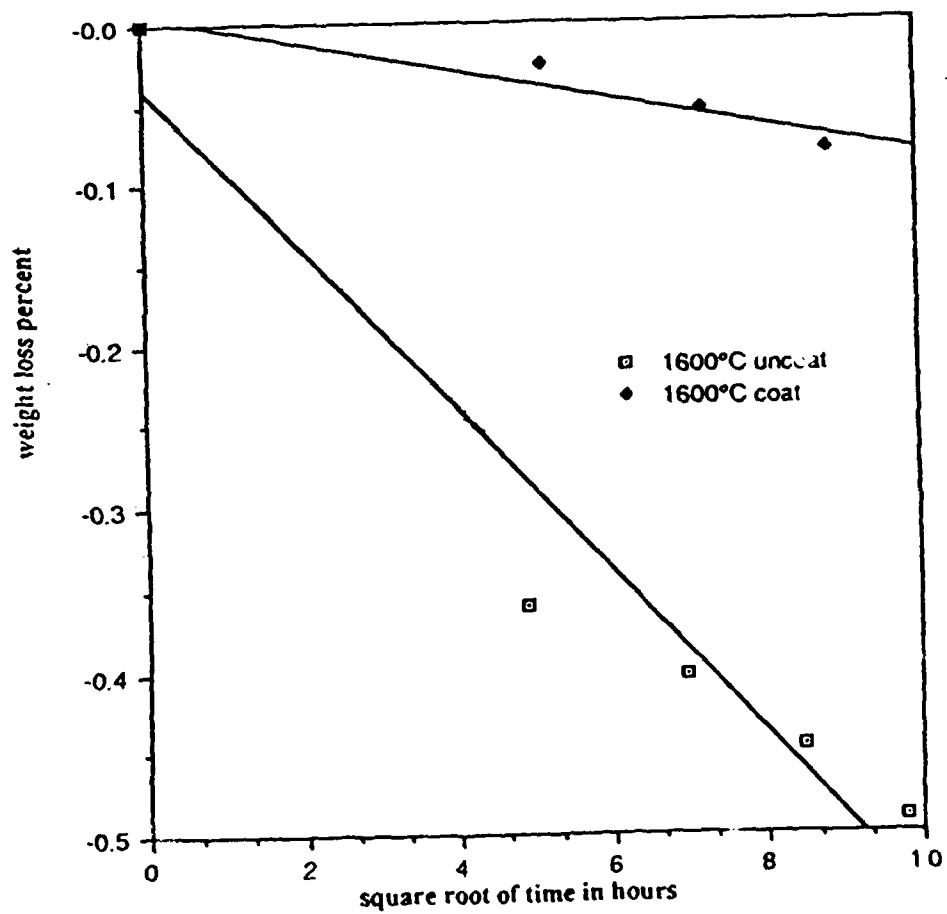
56

Figure 34. Weight loss of coated and uncoated lanthanum chromite heating element at 1600°C versus square root of time.

coated and uncoated samples, the rate being much less in the coated samples. This can be explained by realizing that most of the weight loss is attributed to the vaporization of CrO_3 as discussed by Meadowcroft and Wimmer.[35] Thus in the coated samples any oxygen must diffuse through the alumina to react with the chromium in the lanthanum chromite. In the uncoated samples the only barrier to CrO_3 formation is the bonding of the chromium in the lanthanum chromite structure.

The thermal instability of lanthanum chromite becomes appreciable above 1400°C, due to the vaporization of CrO_3. The alumina coating acts as a diffusion barrier for lanthanum chromite from the oxidizing atmosphere thus minimizing the weight loss. If the lanthanum chromite can be shielded completely from an oxidizing atmosphere by a matrix, then lanthanum chromite would be a suitable composite fiber at 1600°C. However, the matrix could be very hard to identify due to the additional requirement of unreactivity. Although the Japanese used alumina refractories and the samples were coated with alumina, alumina does react with lanthanum chromite.

To gain insight into the extent of the reaction a smooth piece of lanthanum chromite heating element was placed in contact with a piece of dense alumina. The reaction couple was heat treated at 1600°C for 72 hours. The white alumina became visibly pink throughout the piece. However, where intimate contact occurred the alumina became green and almost brown, as shown in Figure 35. The green and pink are probably due to the changes of chromia concentration in the alumina. Energy dispersive X-ray spectroscopy, EDX, was performed on the alumina piece and on the lanthanum chromite piece after the reaction. The EDX showed that the chromium as well as the lanthanum diffused into the alumina. However, the concentration of aluminum in the $LaCrO_3$ piece was less than two percent. This was interesting because the density of the lanthanum chromite was approximately 88 percent, while the density of the alumina piece was greater than 96 percent. X-ray diffraction patterns of the alumina piece in both the pink and green/brown regions reveal many phases, including several lanthanum β – alumina phases as
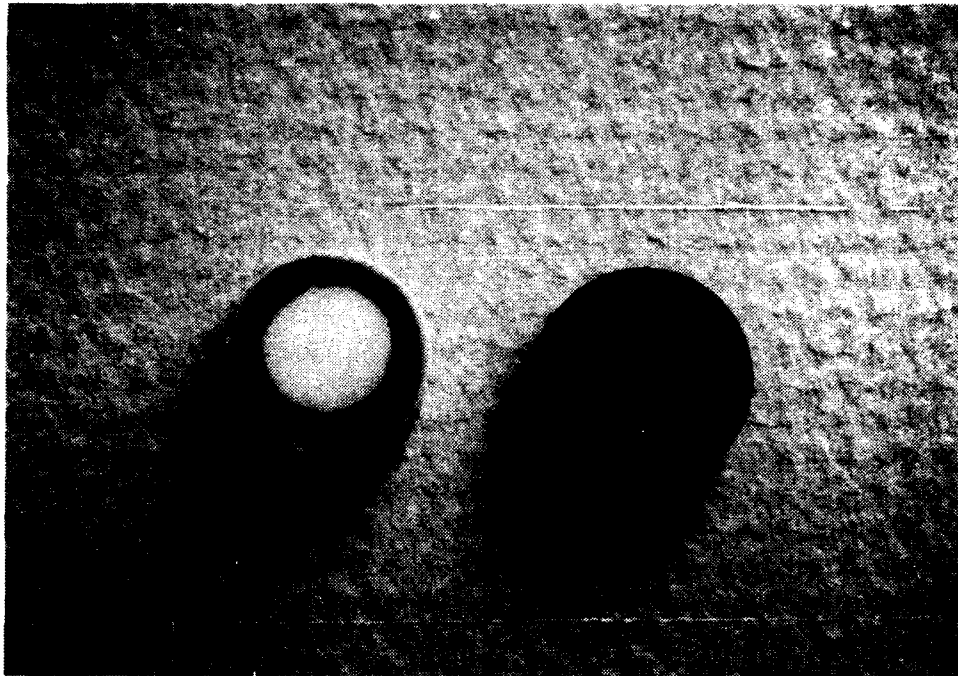
Figure 35   Photograph of a diffusion couple of lanthanum chromite and alumina.
The brown sample is lanthanum chromite, the pink sample with the
green/brown ring is alumina. The color change in the alumina
is due to varying concentrations of chromium and lanthanum.

well as chromium-doped alumina. Further investigations would be necessary to conclude what these reaction products are and whether they are deleterious.

3.3   High Temperature Mechanical Testing of Fibers

One part of this project was to evaluate the high temperature mechanical properties of fibers. The main aim was to construct a testing machine such that a fiber is heated to above 1650°C and tested in tension. Because of the limitation in available materials of construction, this test rig was designed to operate in vacuum only.

The schematic plan of the test rig is shown in Figure 36. Photographs in Figure 37 give general and detailed views of the test setup. This setup was based on Model 2967 Vacuum Furnace, manufactured by Norton Company, Vacuum Equipment Division, Newton Highlands, MA. It consists of hot zone and bell-jar assembly, power supply and control station, and vacuum pumping system. Originally, a 3 inch diameter by 8 inch high tantalum heating element was installed for operation at 2000°C in vacuum. The heating element and surrounding tantalum shields are enclosed within a water-cooled copper container that prevents direct radiation to the 18 inch diameter by 30 inch high metal bell-jar. A 3/16 inch diameter hole at the front allows optical pyrometry of the heating element through a glass window in the bell-jar. A 1-1/2 inch hole was machined in the top surface of the copper container as well as in the top heat shield. The lower part of the tensile test assembly is inserted into the hot zone through this hole. The entire assembly is housed within an evacuated bell-jar. This arrangement is similar to the drawing given in the last Quarterly Report, however, a water-cooled copper block was added immediately below the support plate for the mechanical testing drive mechanism and above the hot chamber of the high temperature furnace. It was needed to reduce the heating due to conduction through the graphite tube that holds the lower grip. A variable speed geared motor supplies the driving force and rotates a micrometer movement, which is connected to the train of the load cell (10 lbf capacity). A fiber under test is bonded to the pull rod (1/8 inch diameter graphite rod) using ceramic cement. The bond will be kept outside the heating zone. The other
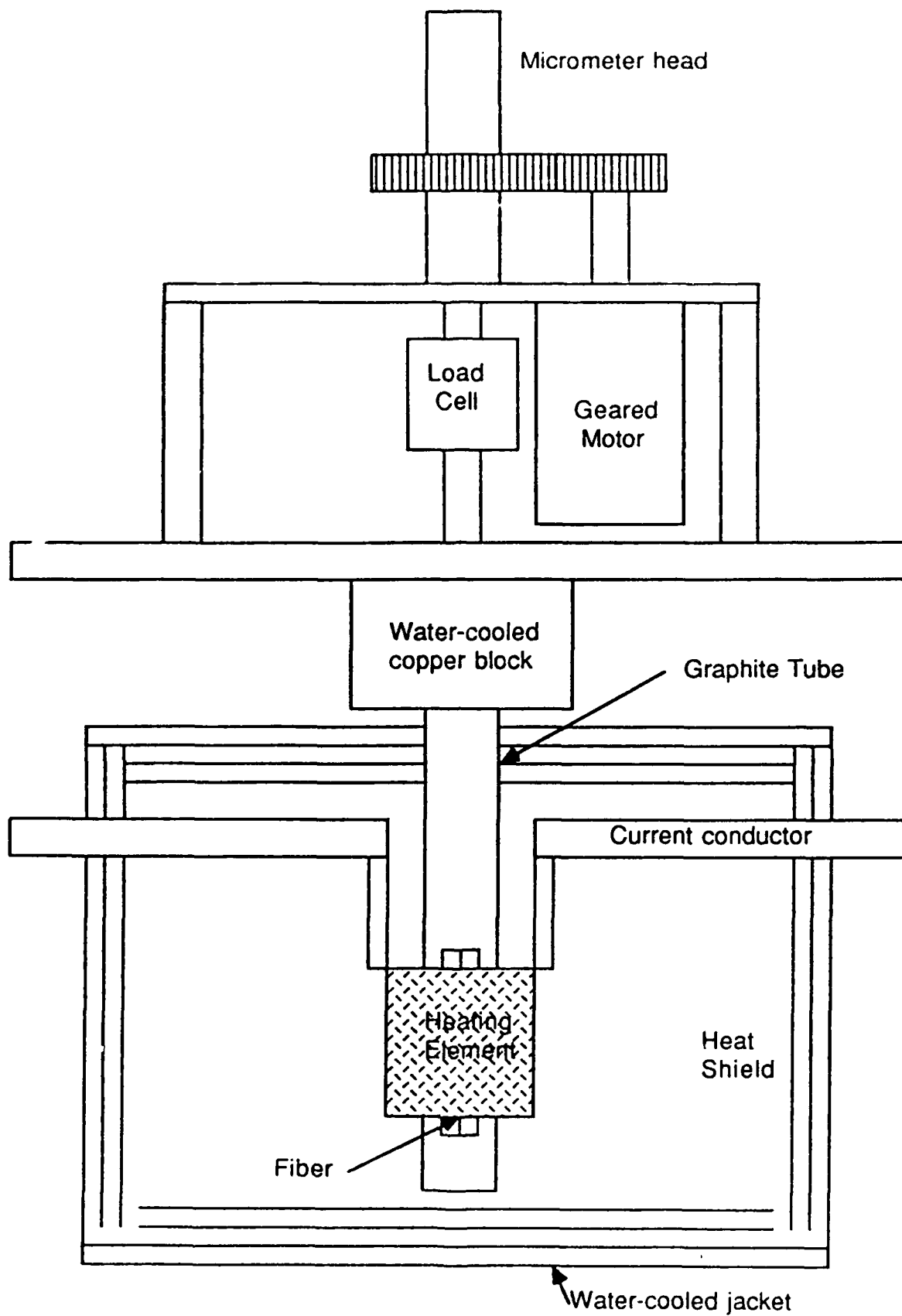
Figure 36   Schematic plan of the high temperature test rig.
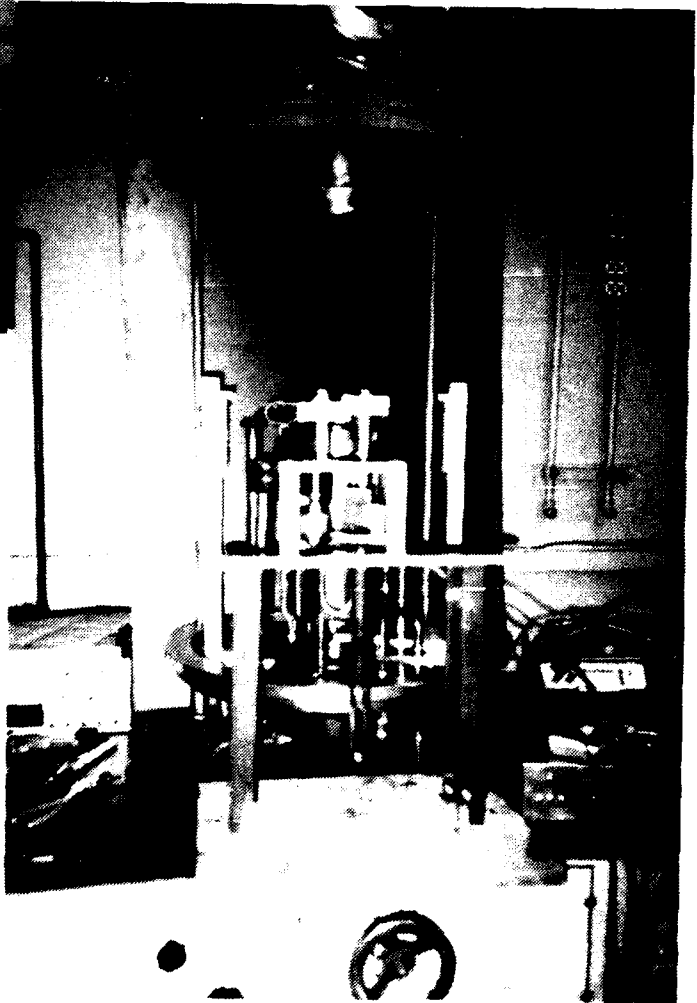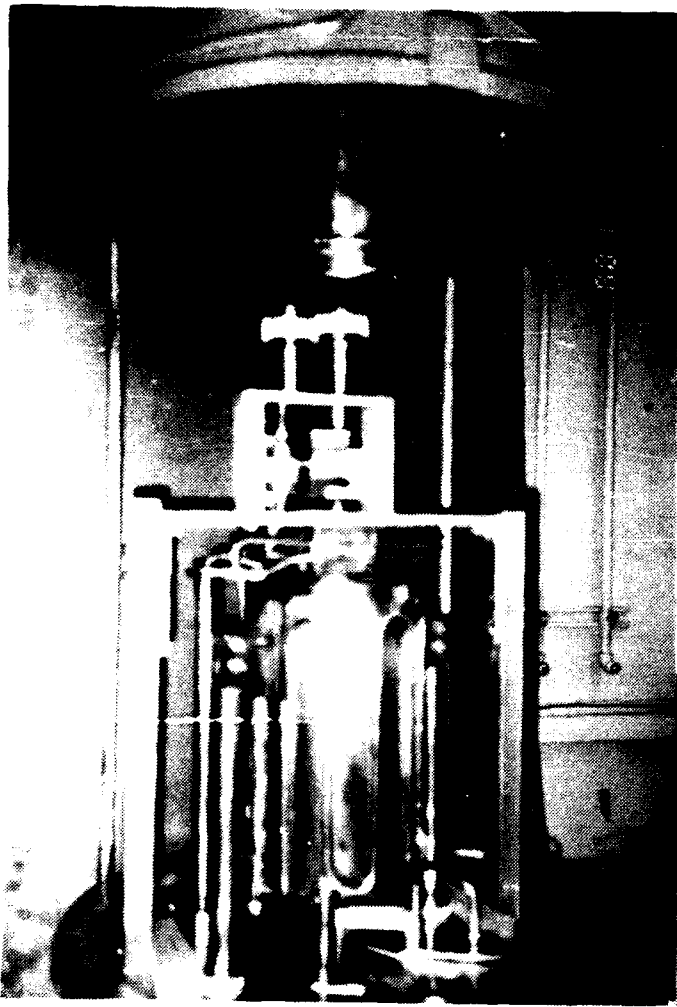
61

Figure 37 Photographs of test setup.

end of the test fiber is bonded to a fixed pull rod attached to the bottom of an outer support, machined from a one inch diameter graphite rod. The pull rod has a fixed speed of 0.025 inch per minute or a variable speed of 0.001 to 0.2 inch per minute. Normally, the fixed speed is used. This setup has been tested in air up to 800°C successfully. Alumina fibers manufactured by Mitsui Mining Co. have been tested. For these fibers, the range of load was between 0.4 and 24 grams. This low range presented no problem for the load cell amplifier employed. Using the constant crosshead speed, the time-axis on a chart recorder can be correlated to total displacement. As is common in testing with an Instron testing machine, no direct strain measurement is made. Since the measurement of total displacement includes extension of pull rod and load cell as well as that of the low temperature segment of the fiber sample, strain measurement of the fiber sample can not be made using the present setup.

Fiber testing inside the vacuum system initially utilized a large heating element (3 inch diameter and 8 inch height). In this case, the entire fiber and grips were inside the hot zone. Tests at room temperature and at 1000°C were conducted. Temperature inside the hot zone was measured using a tungsten-tungsten/rhenium thermocouple. Vacuum of 5×10^{-5} torr or better was maintained during the tests. Some of the results from six tests on Mitsui alumina fibers are given in Table 7.

Table 7 Results of tensile testing of Mitsui alumina fibers using the original heating element.

Sample	Temperature (°C)	Maximum load (g)	Fiber diameter (0.0001 inch)	Tensile strength (ksi)
1	25	10.0	4.63	131.3
2	25	7.8	4.65	101.3
3	25	9.6	6.94	56.6
4	1000	3.75	5.5 (est)	34.8
5	1000	0.35	5.5 (est)	3.2
6	1000	1.0	5.5 (est)	9.3

The gauge length at 25°C was 2 inches, while that at 1000°C was 1.5 inches, respectively. The fiber diameter of the high temperature tests were estimated since the tested fibers could not be recovered. The last two tests at 1000°C are invalid due to fiber fracture in the lower grip. Although a larger number of tests are needed to obtain valid fiber strength data, these show that fibers can be tested using the setup with the original large heating element.

A new tungsten heating element with a reduced hot zone size (1.5 inch diameter and 2 inch height) was manufactured by an outside supplier (Thermal Technology). It was received after a long delay. Additional tests were conducted using this element, which allows the grips to be outside the hot zone and leaves a larger distance between the hot zone and mechanical testing assembly above the water-cooled chamber. With this new heating element along with an optical pyrometer, the setup can achieve fiber temperatures of 2000°C. The rise in load cell temperature, which increases by 40°C within about 30 minutes, is the limitation of this setup. This is, however, adequate for normal tensile testing of fibers, although the zero level of the load scale moves continuously during a test. While the maximum temperature of 2000°C can be reached, several attempts up to now have not produced valid tensile tests due to the loss of fiber strength. The load-crosshead movement diagram is shown in Figure 38. This is for a test of Tyrano fiber at 1300°C. The scale for the load axis was approximately 5 gm per inch and that for the time axis was one inch per minute, corresponding to 0.025 inch of total displacement per inch on the chart. Note the shift in the zero level due to 2°C rise in the load cell temperature. During the test, the heating element temperature was maintained to ±2°C.

We have tested several different fibers using this new setup. The fibers include Tyrano fiber (Si-Ti-C-N-O, made by Ube Industries, distributed by Avco in the US.), Mitsui and DuPont alumina fibers and a carbon fiber (unknown manufacturer, with electroplated nickel coating). Results of this series of tests are given in Table 8. In these tests, the gauge length was 2.5 inches and nominal diameter was used for the fiber diameter.

Figure 38   Load-time curve for a tensile test of Tyranno fiber at 1300°C.
Load: ~ 5 grams/inch; Time: 1 inch/minute.
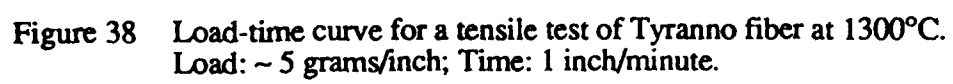
Table 8 Results of tensile testign using the new heating element.

Sample	Temperature (°C)	Maximum load (g)	Fiber diameter (μm)	Tensile strength (ksi)
Carbon -1	25	21.2	7	779
-2	25	7.8	7	286
-3	1000*	11.5	7	425
Alumina - Mitsui Mining				
-1	1000*	1.25	7	46.2
-2	1000*	1.0	7	36.9
-3	1000	1.5	7	55.6
Alumina - DuPont FP				
-1	1000*	16.8	20	75.6
Tyranno -Ube				
-1	1200*	13.5	9	302
-2	1300*	9.0	9	201
-3	1350*	14.8	9	330
-4	1200	7.0	9	157
-5	1300	1.75	9	39.1
-6	1300	2.75	9	61.5
-7	1300	3.0	9	67.1

* Estimated. Actual values were lower by 50 to 100°C.

Additionally, we attempted to test a PAN-based carbon fiber that had no sizing. However, bonding with ceramic cement was poor and no successful test has been completed to date.

From these tests, the test setup functions as designed. Although fiber tensile tests at 2000°C are yet to be performed, ability to attain the maximum design temperature has been demonstrated.

3.3.1 Future Work on Fiber Testing

It is recommended that the unique capability of this high temperature tensile testing setup be utilized in a systematic property evaluation program of various fibers. Correlation of fiber manufacturing processes and high temperature strength should be explored.

4. CONCLUSION

During the past year the research conducted in this project has been separated into three areas: (1) the investigation of lanthanum chromite preparation, (2) the study of lanthanum chromite's high temperature stability, (3) the mechanical testing of sol-gel derived oxide fibers at elevated temperatures. The significant results are listed below.

1. Lanthanum chromite was prepared by several new solution based methods. Pre-ceramic lanthanum chromite precursor fibers were drawn from solution.

2. The stability of lanthanum chromite at high temperatures >1500°C in an oxidizing environment was studied. The stability of the lanthanum chromite was enhanced by coating with alumina, thus minimizing the vaporization of chromia.

3. A miniature tensile testing machine housed within a high vacuum system was constructed. Fiber tensile tests up to 1300°C have been performed. The heating capability of the setup to 2000°C has been demonstrated.

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